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## Feature Article

# Structuring adsorbents and catalysts by processing of porous powders<sup>☆</sup>

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## Abstract

Microporous materials such as zeolites, metal organic frameworks, activated carbons and aluminum phosphates are suitable for catalysis and separation applications. These high surface area materials are invariably produced in particulate forms and need to be transformed into hierarchically porous structures for high performance adsorbents or catalysts. Structuring of porous powders enables an optimized structure with high mass transfer, low pressure drop, good heat management, and high mechanical and chemical stability. The requirements and important properties of hierarchically porous structures are reviewed with a focus on applications in gas separation and catalysis. Versatile powder processing routes to process porous powders into hierarchically porous structures like extrusion, coatings of scaffolds and honeycombs, colloidal processing and direct casting, and sacrificial approaches are presented and discussed. The use and limitations of the use of inorganic binders for increasing the mechanical strength is reviewed, and the most important binder systems, e.g. clays and silica, are described in detail. Recent advances to produce binder-free and complex shaped hierarchically porous monoliths are described and their performance is compared with traditional binder-containing structured adsorbents. Needs related to better thermal management and improved kinetics and volume efficiency are discussed and an outlook on future research is also given.

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**Keywords:** Porous powder; Structuring; Gas separation; Catalysis

## 1. Introduction

Porous materials with porosities in the microporous (smaller than 2 nm), mesoporous (between 2 and 50 nm) and macroporous (larger than 50 nm) range<sup>1</sup> are extensively used for applications in catalysis, separation and filtration. Microporous and mesoporous compounds are researched as materials with potential applications in e.g. ion exchange,<sup>2</sup> separation and catalysis,<sup>3</sup> insulation,<sup>4,5</sup> drug delivery,<sup>6</sup> sensors,<sup>7</sup> lasers,<sup>8</sup> low-*k* substrates for electronic application,<sup>9,10</sup> and as electrode materials in e.g. batteries<sup>11</sup> and fuel cells.<sup>12</sup> Macroporous inorganic

compounds, on the other hand, are studied as materials in high temperature applications, e.g. filtration of molten metal,<sup>13</sup> refractory insulation<sup>14</sup> and hot gas filtration,<sup>15</sup> and as heating elements<sup>16</sup> but are also researched for low temperature applications e.g. as scaffolds for bone replacement.<sup>17,18</sup>

Porous inorganic materials are alternatives to polymer-based ion exchange resins, e.g. for water softening<sup>19</sup> that include the exchange of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Na}^+$  and the removal of toxic heavy metals from waste streams<sup>20,21</sup> and radioactive waste management.<sup>22</sup> The applications of porous materials to catalysis are numerous, where either the material acts as a support or is functional itself. The applications range from exhaust control in cars and trucks to various applications in refinery chemistry such as hydroisomerization and olefin production.<sup>23</sup> Industrially important separation processes include drying of air<sup>24</sup> and liquids,<sup>25</sup> separation of oxygen/nitrogen from air,<sup>26</sup> purification of  $\text{H}_2$ <sup>27</sup> aromatic separation,<sup>28</sup> liquid paraffin separation<sup>29</sup> and considerable attention has recently been given to carbon dioxide ( $\text{CO}_2$ ) capture from flue gas,<sup>30,31</sup> and biogas upgrading.<sup>32</sup>

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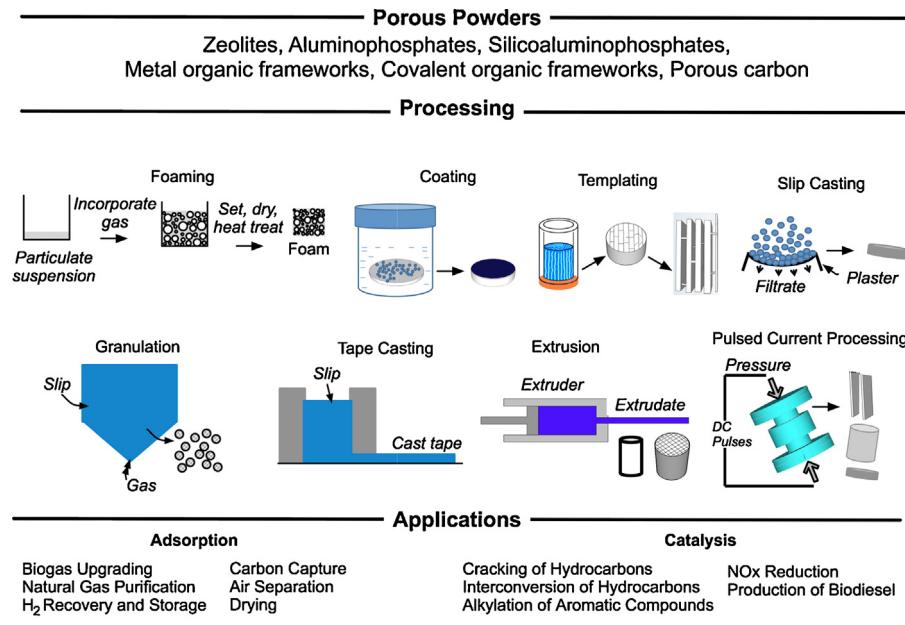


Fig. 1. Overview of the main types of porous powders, the important processing routes and examples of industrial applications of structured adsorbents and catalysts.

Applications in gas separation and catalysis utilize microporous materials with very high surface areas including, zeolites, metal organic frameworks (MOFs), aluminum phosphates, silicoaluminophosphates, and activated carbons and porous polymers. Typically, the inorganic structures of zeolites are highly stable to temperature variations. Microporous aluminophosphates (AlPO<sub>4</sub>s) and silicoaluminophosphates (SAPOs) have structures that are very similar to those of microporous zeolites but are usually somewhat less hydrophilic. MOFs are crystalline porous structures with tunable pore sizes constructed from metal ions that are coordinated by rigid and aromatic organic linkers. Activated carbons, produced from carbon-rich precursors by chemical and physical activation, are highly porous hydrophobic materials with very small pores and narrow pore size distribution.

Effective utilization of microporous materials in applications in gas separation and catalysis requires that the microporous powder is structured into a macroscopic shape. This shape should have a sufficient mechanical, chemical and attrition resistance and a structure that promotes high flows and rapid mass transfer.<sup>33,34</sup> Despite the high industrial importance of producing structured adsorbents and catalysts from porous powders, there are only few articles in the academic literature directly addressing structuring. Traditionally, structuring of catalysts and adsorbents has been developed by the dominating companies and kept as in-house know-how or only disseminated in patents. However, the rapidly growing interests in microporous materials for emerging applications like hydrogen<sup>35</sup> and methane<sup>36</sup> storage, green catalysis,<sup>37</sup> and carbon capture<sup>31</sup> have also resulted in an increased amount of open research in structured adsorbents and catalysts. Indeed, carbon capture using adsorbents has been suggested as one of the prime candidates to the potential need of annually treating several gigatons of flue gas to alleviate the release of anthropogenic carbon dioxide into the atmosphere.<sup>38</sup> Zeolites can be used in applications in gas separation and

catalysis if they are structured into beads, granules or pellets. Often this structuring is achieved by using processing techniques including extrusion, spray-drying or granulation. The zeolite powder is first mixed with an inorganic and organic binder, then shaped into the desired geometry, and finally thermally treated to remove the organic binder and impart mechanical strength by the inorganic binder. However, the high pressure drops associated with a flow through packed beds of beads or pellets, and mass transfer limitations related to slow diffusion in and out of the granules or pellets are limiting the performance, in particular for large-scale applications. Therefore, structuring of adsorbents and catalysts in more complex geometrical configurations, e.g. foams, honeycombs, monoliths, laminates, that can demonstrate rapid process dynamics has recently attained considerable interest as more efficient alternatives to traditional pellets and granules (Fig. 1).

Processing of powders is a well-established area in the ceramic field and recent reviews by e.g. Studart et al.<sup>17</sup> and Colombo<sup>18</sup> have described how macroporous and cellular ceramics can be produced from non-porous ceramic powders. This review will describe and discuss the processing of porous powders into hierarchically porous or structured materials. Solution-based routes for mesoporous and micro-porous materials, including the synthesis of hierarchically porous zeolites<sup>39</sup> have recently been covered in detail<sup>40,41</sup> and will not be dealt with here. The structural characteristics of the dominating classes of porous powders – zeolites, AlPO<sub>4</sub>s and SAPOs, activated carbons and carbon molecular sieves (CMSs), MOFs, covalent organic frameworks (COFs) and microporous polymers – are described together with the useful properties primarily for applications in gas separation. Important transport and thermal properties of adsorbents and catalysts are related to the structural requirements of the hierarchical porous structure and its specific design. The various processing routes to produce structured adsorbents from porous

Table 1

A summary of widely used porous materials in gas separation and catalysis.

Material	Application	Refs.
<i>Hydrophilic zeolites</i>		
Zeolite X	CO <sub>2</sub> capture, air separation, production of biodiesel	Bae et al., <sup>69</sup> Leavitt et al., <sup>107</sup> Babajide et al., <sup>63</sup>
Zeolite A	H <sub>2</sub> purification, dehydration, cracking of gas oils	Li et al., <sup>108</sup> Xu et al., <sup>109</sup> Al-Mayman et al. <sup>110</sup>
Zeolite-rho	Air separation, conversion of methanol and ammonia to dimethylamine	Corbin, <sup>111</sup> Abrams et al. <sup>112</sup>
<i>Hydrophobic zeolites</i>		
Silicalite	Paraffin separation, gas-phase ketonisation of propionic acid	Kulprathipanja et al., <sup>113</sup> Bayahia et al., <sup>114</sup>
SSZ-13	Hydrocarbon separation, reduction of NO <sub>x</sub>	Reyes et al., <sup>115</sup> Martinez-Franco et al. <sup>116</sup>
ZSM-5	Xylene separation, interconversion of hydrocarbons and alkylation of aromatic compounds	Daramola et al., <sup>28</sup> Milton et al. <sup>50</sup>
<i>Silicoaluminophosphates</i>		
SAPO-56	CO <sub>2</sub> capture, catalytic cracking of hydrocarbons, methanol to olefin	Cheung et al., <sup>102</sup> Pellet et al. <sup>117</sup>
SAPO-34	CO <sub>2</sub> –H <sub>2</sub> , N <sub>2</sub> –H <sub>2</sub> separation, catalytic cracking of hydrocarbons, methanol to olefin	Das et al., <sup>118</sup> Pellet et al. <sup>117</sup>
AlPO <sub>4</sub> s	CO <sub>2</sub> capture, synthesis of isoprene	Liu et al., <sup>43</sup> Hutchings et al., <sup>99</sup>
<i>Microporous carbons</i>		
VR-93	CO <sub>2</sub> capture	Silvestre-Albero et al., <sup>119</sup>
Activated carbon	CH <sub>4</sub> , CO <sub>2</sub> and N <sub>2</sub> separation, hydroxylation of phenols; H <sub>2</sub> S removal	Ribeiro et al., <sup>120</sup> Li et al. <sup>121</sup>
<i>Metal–organic frameworks</i>		
Mg-MOF-77	CO <sub>2</sub> capture	Mason et al. <sup>122</sup>
Mg <sub>3</sub> (ndc) <sub>3</sub>	O <sub>2</sub> –N <sub>2</sub> , N <sub>2</sub> –H <sub>2</sub> separation	Dinca et al. <sup>123</sup>
Mmen-CuBTTri	CO <sub>2</sub> capture	McDonald et al. <sup>124</sup>
MOFs	Cyano-silylation of benzaldehyde or acetone, oxidation of olefins, hydroxylation of both linear and cyclic alkanes, epoxidizing of olefins.	Lee et al. <sup>125</sup>

powders are described in detail. The structural flexibility and limitations of extrusion of pellets and honeycombs, sacrificial templating, colloidal processing and direct casting, and coating of scaffolds and honeycombs on feature sizes are exemplified and discussed. The common industrial practice of using inorganic binders for increasing the mechanical strength is reviewed, and the most important binder systems are described in detail. Recently developed routes to avoid diluting the active material with inert binders through so-called binder-less processing is described. Finally, an outlook on novel processing routes and new applications is given.

## 2. Properties and structural characteristics of microporous materials with a focus on gas separation

The industrially important microporous materials for applications in separation and catalysis include zeolites,<sup>38</sup> MOFs,<sup>42</sup> AlPO<sub>4</sub>s,<sup>43</sup> activated carbons and CMSs.<sup>44–47</sup> In this section, we provide a brief description of the structure, composition, synthesis and some key properties of the different porous solids and elaborate in more detail on their use for effective separation of gases (Table 1).

### 2.1. Zeolites

Zeolites are crystalline aluminosilicates with molecule-sized pores or pore channels and high specific surface areas. The ordered zeolite pores (typically 2.5–10 Å) enable the separation

of gases<sup>48</sup> and catalytic transformations of small molecules.<sup>39</sup> The inorganic crystalline structures of zeolites are highly stable to temperature variations, and their catalytic and adsorption properties render them useful in various industrial and household applications. In most applications synthetic zeolites are used. Typically, reactants that act as silicon and aluminum sources are first mixed with an organic template in water. Thereafter the mixture is heated under hydrothermal conditions for a designated time, after which the initially amorphous gel has transformed into crystals. The crystals are thereafter “calcined” to remove the organic template. Organotemplate-free or green zeolite synthesis routes avoid the use of organic templates and include the addition of zeolite seeds to the starting gels.<sup>49</sup> Despite extensive research efforts, the reaction mechanisms remain a matter of extensive debate, see e.g. the review by Cundy and Cox.<sup>41</sup>

The advantages of using zeolites in applications for gas separation and catalysis lie in their internal framework structure and chemistry, and the relatively low cost. For instance, the internal framework structures of many zeolites carry negative charges that are balanced by extra framework cations. These cations lead to large internal electrical field gradients that can interact strongly with the molecules that possess a large electric quadrupole moment. Hence, this interaction can facilitate the transformation and separation of these molecules, e.g. the separation of CO<sub>2</sub> from N<sub>2</sub> in flue gas. Furthermore, zeolites offer possibilities of pore engineering to separate molecules on the basis of size.<sup>48</sup>

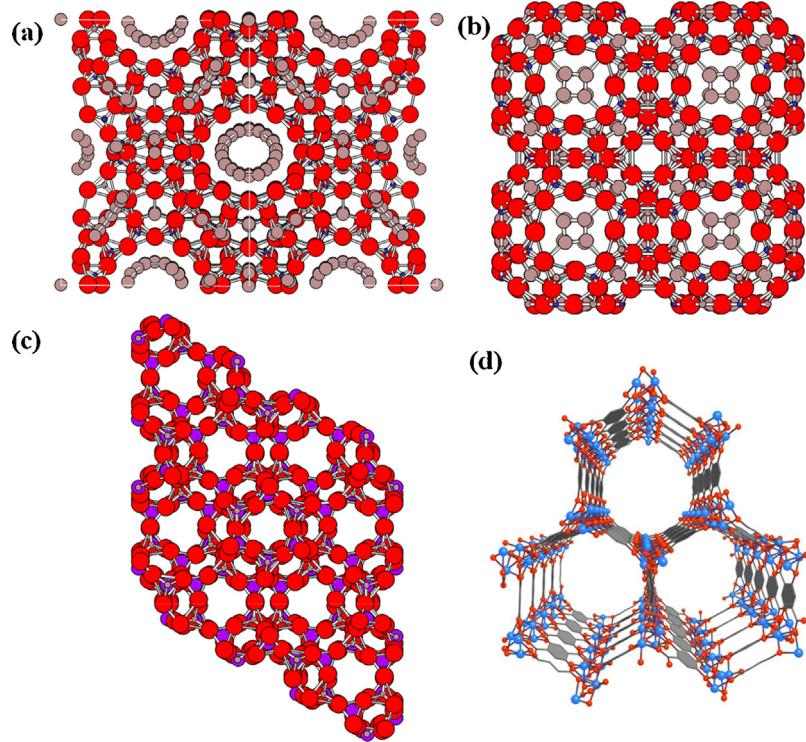


Fig. 2. Structures of microporous materials: (a) framework code FAU, viewing direction [1 1 0]; zeolite 13X, ● – Si, ■ – Al, ● – Na, ● – O, (b) framework code LTA, viewing direction [1 0 0]; zeolite 4A, ● – Si, ■ – Al, ● – Na, ● – O, (c) framework code AFX, viewing direction [0 0 1]; SAPO-56, ■ – Al, ● – P, ● – O and (d) structure of Mg-MOF-74.<sup>106</sup>

Zeolite NaX is the standard adsorbent researched for CO<sub>2</sub> removal from flue gas. This sodium aluminumsilicate has a Si-to-Al ratio of 1:3<sup>50</sup> and its structure consists of porous cages that are connected with pore window apertures encircled by 24 atoms (12 oxygen atoms), see Fig. 2a. Adsorbed CO<sub>2</sub> and N<sub>2</sub> can generally diffuse relatively unhindered throughout zeolite NaX as its apertures are larger than the kinetic dimensions of both CO<sub>2</sub> and N<sub>2</sub>. The isosteric heat of adsorption of CO<sub>2</sub> on zeolite NaX is high: 50–60 kJ/mol.<sup>51–54</sup> Note that CO<sub>2</sub> mainly physisorbs on NaX, but the chemisorption is also significant.<sup>55</sup> Brandi and Ruthven showed that co-adsorbed water on zeolite NaX appeared to reduce the electrical field gradients and, hence, reduce the tendencies to CO<sub>2</sub> adsorption.<sup>56</sup> Zeolite LiX is an important adsorbent for air separation.<sup>57</sup> Zeolite LiX adsorbs N<sub>2</sub> more strongly than O<sub>2</sub>. Li<sup>+</sup>, amongst the cations, provide the strongest interactions with the quadruple moment of N<sub>2</sub> molecule due to its high polarizing power (i.e. charge/ionic radius).<sup>58</sup> The strong interaction between Li cation and N<sub>2</sub> molecule results in a high adsorption of nitrogen and a good air separation performance.<sup>59</sup> NaX is exchanged partially with cesium ions to prepare oxygen selective Na–CeX adsorbent for air separation.<sup>60</sup> In a study by Air products, CaX was reported to exhibit high nitrogen capacity and selectivity for air separation.<sup>61</sup> Zeolites X modified by alkali ion exchange has emerged as an appealing heterogeneous catalyst, e.g. in the production of biodiesel, since relatively weak basic sites and strong basic sites can be produced via alkali metal ion exchange and impregnation of basic components, respectively.<sup>62,63</sup>

Zeolite Y has the same general caged structure as Zeolite X with the structural code of FAU.<sup>64</sup> Its framework structure has a Si-to-Al ratio of 2:3. Walton et al.<sup>65</sup> compared the CO<sub>2</sub> sorption for different versions of zeolite X and Y. They reported that the capacity to CO<sub>2</sub> sorption of both zeolite X and Y increased with decreasing ionic radii of the balancing cations in the zeolite framework. Li-exchanged zeolite X and Y displayed the highest observed capacities to adsorption of CO<sub>2</sub>, respectively. Zeolite Y has been the primary active material of fluid catalytic cracking (FCC) catalyst for the cracking of heavy hydrocarbons.<sup>66</sup> “Ultrastable zeolites Y” – USY are prepared by treating ammonium-exchanged zeolite Y in 100% steam at a temperature up to 800 °C. The preparation process partially dealuminates the framework and creates extra-framework aluminum (weak Lewis acid centers) while the aluminum in the framework creates (strong Brønsted acid) sites necessary for cracking. The creation of mesoporosity improves the catalytic cracking performance of USY owing to the enhanced diffusivity of large molecules to the acid centers.<sup>67,68</sup>

Zeolite A is an aluminum-rich zeolite with porous cages that have pore windows that are very narrow and encircled by 16 atoms (8 oxygen atoms). Its structure is displayed in Fig. 2b. Most versions of zeolite A have a large capacity to adsorb CO<sub>2</sub> at the low partial pressures of CO<sub>2</sub> that is present in flue gas. Hence, numerous authors have recently chosen to revisit and restudy the adsorption of CO<sub>2</sub> and N<sub>2</sub> on zeolite A.<sup>69,70,71,72,73,74</sup> Zeolite MgA showed excellent properties for a hypothetical adsorption driven separation of CO<sub>2</sub> from dry flue gas.<sup>75</sup> Zeolite A can also be modified for catalytic applications. Zhan et al.<sup>76</sup> reported

the encapsulation of RuO<sub>2</sub> within zeolite NaA by a hydrothermal synthesis method. The supported catalyst would be used to oxidize methanol preferentially over 2-methyl-1-propanol. Verboekend et al.<sup>77</sup> prepared a hierarchical zeolite A type catalyst by alkali ion exchange (Cs, Na) or by high temperature nitridation in ammonia for knoevenagel condensation of benzaldehyde with malononitrile.

Chabazite has very narrow pore window apertures that are encircled by 16 atoms (8 oxygen atoms). In its native form it has a silicon-to-aluminum ratio of 2 and displays very significant capacities to adsorb CO<sub>2</sub> at low partial pressures. In its Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> ion-exchanged forms, it has been studied for its ability to selectively adsorb CO<sub>2</sub> over N<sub>2</sub>.<sup>78–84</sup> Chabazite zeolite, modified with Cu, Fe or Co is an industrially important catalyst, used to reduce NO<sub>x</sub> from exhaust gas streams from gasoline and diesel engines.<sup>85</sup> Zeolite ZK-5 (with the Framework Type Code: KFI) is another 8-ring zeolite that has been shown to have a high capacity to adsorb CO<sub>2</sub> and to have a high CO<sub>2</sub>-over-N<sub>2</sub> selectivity.<sup>86</sup> In general the hydrophilic zeolites display very promising properties for capture of CO<sub>2</sub> from bone-dry gas mixtures.

Zeolites with a high silicon-to-aluminum ratio are hydrophobic. These silicon-rich zeolites could be highly promising candidates for CO<sub>2</sub> capture from moist gases. Lively et al.<sup>87</sup> predicted a smaller cost for CO<sub>2</sub> capture using such a hydrophobic zeolite (MFI) as compared with hydrophilic zeolites (13X) and supported amines. They compared the minimal energy cost under excessive heat integration. Zeolite ZSM-5 with the structural code of MFI is a good example of a heterogeneous catalyst used for the inter-conversion of hydrocarbons and alkylation of aromatic compounds.<sup>88</sup> Hierarchical zeolite ZSM-5 has been reported with extended lifetime and high selectivity compared to conventional zeolite in conversion of methanol-to-olefins.<sup>89</sup> García-Pérez et al.<sup>90</sup> concluded that microporous silicates with structural codes of MFI, MOR, ISV, ITE, CHA, and DDR all displayed high CO<sub>2</sub>-over-N<sub>2</sub> selectivities; these selectivities were expected to be even higher for slightly protonated versions with some aluminum atoms present in the framework. They derived their conclusions by comparing the adsorption of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> on all-silica microporous materials with zeolitic structures. SSZ-13 with its high silicon-to-aluminum ratio<sup>91,92</sup> is such a possible candidate sorbent for an adsorption-driven separation of CO<sub>2</sub> from humid flue gas. It is a high-silica equivalent of the chabazite structure (CHA).<sup>93,94</sup> Microporous silicates with the structural code of DDR have been studied in detail for the CO<sub>2</sub>-over-CH<sub>4</sub> selection,<sup>95</sup> but could indeed be relevant for an enhanced CO<sub>2</sub>-over-N<sub>2</sub> selection, perhaps especially at a somewhat reduced temperature.<sup>96,97</sup>

## 2.2. Aluminum phosphates (AlPO<sub>4</sub>s) and silicoaluminophosphates (SAPOs)

Microporous AlPO<sub>4</sub>s and SAPOs have structures that are similar to those of microporous silica materials and zeolites, respectively. AlPO<sub>4</sub>s are typically synthesized by hydrothermal reactions using an aluminum source (for example aluminum isopropoxide), phosphoric acid, and a suitable amine based organic

template. The organic templates are removed in a subsequent “calcination” step. In SAPOs, some phosphorous atoms are replaced with silicon atoms, which give the framework a net negative charge, much in the same way as aluminum is giving zeolitic frameworks their negative charge. SAPOs are typically synthesized by hydrothermal reactions, as for AlPO<sub>4</sub>s, but with the addition of a silica source.<sup>98</sup>

AlPO<sub>4</sub>s have no extra framework cations and have smaller internal electrical field gradients than SAPOs and zeolites. They are, hence, rather hydrophobic. Liu et al.<sup>43</sup> studied a range of such AlPO<sub>4</sub>s with very small pore window apertures. Some of those AlPO<sub>4</sub>s displayed a significant CO<sub>2</sub>-over-N<sub>2</sub> selectivity, which was related to kinetic contributions. The adsorption of CO<sub>2</sub> on those AlPO<sub>4</sub>s was somewhat smaller than expected, which could have related to sample quality. Hutchings et al.<sup>99</sup> reported the synthesis of isoprene from dehydration of 2-methylbutanal using AlPO<sub>4</sub> and mixed boron/AlPO<sub>4</sub> catalyst. They showed that the AlPO<sub>4</sub> catalyst was suitable for the synthesis of isoprene from methyl isopropyl ketone, which is a major by-product from the reaction of 2-methylbutanal.

Li et al.<sup>100</sup> studied the adsorption of CO<sub>2</sub> and N<sub>2</sub> on SAPO-34 in the context of its use as a membrane for natural gas processing. Araki et al.<sup>101</sup> contrasted those findings with the adsorption of CO<sub>2</sub> and N<sub>2</sub> on zeolite rho and conclude that zeolite rho displayed a higher CO<sub>2</sub>-over-N<sub>2</sub> selectivity than did both SAPO-34 and zeolite 13X, although with a comparably smaller capacity for adsorption of CO<sub>2</sub>. Cheung et al.<sup>102</sup> recently showed that SAPO-56, with 8-ring apertures, displayed a very high capacity to adsorb CO<sub>2</sub>, Fig. 2c. Cu and Fe based SAPOs catalysts have been demonstrated as being promising NO<sub>x</sub>-SCR catalysts in industry.<sup>103,104</sup> SAPOs are patented as catalytic cracking catalysts for cracking hydrocarbon feed stock.<sup>105</sup> Modifications of SAPOs to achieve unique silicon distributions showed high performance in cracking of hydrocarbons.<sup>105</sup>

## 2.3. Activated carbons, carbon molecular sieves and metal organic frameworks

Activated carbons can be produced from carbon-rich precursors by chemical and physical activation.<sup>126</sup> Under physical activation, the carbon-rich precursor is treated with air, carbon dioxide or steam at a high temperature. During chemical activation, the carbon-rich precursor is first mixed with strong bases or acids (e.g. KOH, ZnCl, or H<sub>3</sub>PO<sub>4</sub>) and then subsequently subjected to an elevated temperature under a flow of nitrogen. The pore size distributions of the resulting activated carbons are strongly dependent on the type of activation used, the process conditions, as well as the type and origin of the carbon-rich precursors. Carbon molecular sieves (CMSs) are porous carbons with very small pores and narrow pore size distribution. Traditionally, the term CMS is used for porous carbons with narrow pore apertures that are produced from an activated carbon by chemical vapor deposition of aromatic molecules that are subsequently pyrolyzed.<sup>127</sup>

Activated carbons have high capacities for CO<sub>2</sub> sorption and are more tolerant to water in the flue gas than zeolites; hence, they are attractive as CO<sub>2</sub> sorbents. Radosz et al.<sup>44</sup> studied how

Table 2

Materials properties of three different microporous materials.

Material	Zeolite 13X	AlPO-18	MOF 5
Density (kg/m <sup>3</sup> )	1470 <sup>149</sup>	2560 <sup>150</sup>	605 <sup>151</sup>
Nominal pore opening (nm)	0.75 <sup>149</sup>	0.46 <sup>152</sup>	1.2 <sup>153</sup>
Elastic modulus (GPa)	50 <sup>154</sup>	–	18.5 <sup>155</sup>
Coefficient of thermal expansion (1/K)	$\alpha_L (-4.2 \times 10^{-6})^{156}$	$\alpha_v (-26.04 \times 10^{-6})^{157}$	$\alpha_L (-13.1 \times 10^{-6})^{158}$
Thermal conductivity at 300 K (W/m K)	2.0 <sup>159</sup>	–	0.31 <sup>160</sup>
Heat capacity (kJ/kg K)	1.34 <sup>161</sup>	0.7 <sup>150</sup>	1.4 <sup>162</sup>
CO <sub>2</sub> uptake capacity at 293 K at 1 bar (mol/kg)	5.8 <sup>73</sup>	1.4 <sup>43</sup>	1.1 <sup>163</sup>
N <sub>2</sub> uptake capacity at 293 K at 1 bar (mol/kg)	0.6 <sup>73</sup>	0.1 <sup>43</sup>	–
H <sub>2</sub> O uptake capacity at 293 K at 1 bar (mol/kg)	20 <sup>43</sup>	12 <sup>43</sup>	Only up to 4 wt.% <sup>164</sup>
Heat of N <sub>2</sub> adsorption (kJ/mol)	17 <sup>161</sup>	–	5 <sup>165</sup>
Heat of CO <sub>2</sub> adsorption (kJ/mol)	37 <sup>52</sup>	26 <sup>166</sup>	15 <sup>165</sup>
Heat of H <sub>2</sub> O adsorption (kJ/mol)	80 <sup>167</sup>	55 <sup>168</sup>	–
Thermally Stable up to a temperature of (°C)	800 <sup>169</sup>	900 <sup>170</sup>	350 <sup>171</sup>

regular activated carbons could be used in a particular capture process and showed that the carbons exhibited high capacity and high CO<sub>2</sub>-over-N<sub>2</sub> selectivities. For a partial pressure of CO<sub>2</sub> of 0.1 bar and a temperature of 40–50 °C, carbons with significant amounts of ultra-micropores (0.3–0.5 nm) appeared to be most relevant for carbon capture. Presser et al.<sup>45</sup> showed that at 10 kPa, pores smaller than 0.5 nm are most preferred. Similar tendencies that the CO<sub>2</sub> adsorption is enhanced by small pores have been observed by others.<sup>128–131</sup> Activated carbons with basic surface functionalities show a high uptake of CO<sub>2</sub>, for example reported by Arenillas et al.<sup>132</sup> We expect further research on carbon materials that combine the possibility for weak chemisorption with narrow pores for a selective uptake of CO<sub>2</sub> at low partial pressures.

Porous carbon is an important substrate material for catalysts due e.g. to the inertness to acid and redox agents, high stability under reaction conditions, good mass transfer properties, high mechanical integrity and low cost. Also pure carbon materials such as activated carbon<sup>133</sup> and multi-wall carbon nanotube<sup>134</sup> can be used as catalyst by them self, for example they show excellent catalytic properties for partial oxidation of benzene by H<sub>2</sub>O<sub>2</sub>.<sup>134</sup> Li et al.<sup>121</sup> used microporous carbon based catalysts treated with mixture of hydrofluoric acid and hydrochloric acid and successively with 30% H<sub>2</sub>O<sub>2</sub> for the hydroxylation of phenols. Activated carbons have been used for wet air oxidation.<sup>135–137</sup>

MOFs, COFs, and microporous polymers are three emerging classes of adsorbents that are studied in detail for their potential use as adsorbents for CO<sub>2</sub> capture. MOFs and COFs are crystalline porous structures with tunable pore sizes and they typically have interconnected pores. MOFs are constructed from metal ions that are coordinated by rigid and often aromatic organic linkers (Fig. 2d). MOFs have been intensely researched during the last decade.<sup>138</sup> COFs lack the metal ions and the framework is truly covalent.<sup>139,140</sup> Microporous polymers are a general term that sometimes includes COFs as well as amorphous polymeric frameworks<sup>141</sup> that display pores smaller than 2 nm. Numerous studies of MOFs,<sup>122,142,143</sup> COFs,<sup>144</sup> and microporous polymers<sup>145</sup> have focused on their potential use as CO<sub>2</sub> sorbents. When reflecting over such studies it appears as, it is not the specific surface area that is most crucial for their

properties as potential CO<sub>2</sub> sorbents. Instead, it appears to be the ultra-micropore volume or the heat of adsorption that define their prospects in this respect. Here, we highlight that the MOFs amine-modified CuBTTr<sup>124</sup> and in particular MgMOF-74,<sup>106</sup> Fig. 2d, appear in particular to be promising as CO<sub>2</sub> sorbents for flue gas capture. In addition, the highly selective porous polymer with amine moieties that Lu et al.<sup>146</sup> recently reported, appears to be very promising. MOFs have been proposed and demonstrated for heterogeneous catalysis.<sup>125,147,148</sup> Lee et al.<sup>125</sup> have critically analyzed MOFs and described various possibilities to use MOFs as catalysts. At the moment, it is difficult to judge if these somewhat exotic microporous materials could ever be used for large scale gas separation or as catalysts, or if they should be primarily seen as model materials (see Table 2).

### 3. Requirements and properties of structured adsorbents and catalysts

The performance of structured adsorbents or catalysts is based on the interplay of several parameters including mass and heat transfer properties, gas diffusion kinetics, pressure drop across the adsorbent, mechanical strength and volumetric efficiency, illustrated in Fig. 3. High mechanical integrity of the structured porous materials is critical to the performance in processes where the pressure variations are large and rapid, or when thermal cycling induces stress. The chemical durability of the adsorbents and catalysts is related to the corrosion or deterioration during use and may determine the life-time.<sup>172–174</sup> During gas separation and catalytic processes heat waves develop in the beds and a poor heat transfer from the porous material can adversely affect the separation and catalytic performance. The high pressure drop and a poor mass transfer typical for a conventional bed of granulated or beaded adsorbents have to be minimized for the ultra-rapid swing sorption processes that are needed for large scale applications like CO<sub>2</sub> capture. These limitations can be partially overcome by designing and producing structured adsorbents and catalysts with tailor-made porosity, shape, mass and heat transfer characteristics and high mechanical stability.<sup>34,175</sup> We will revisit aspects of mass and heat transfer, diffusion, pressure drop and geometrical factors

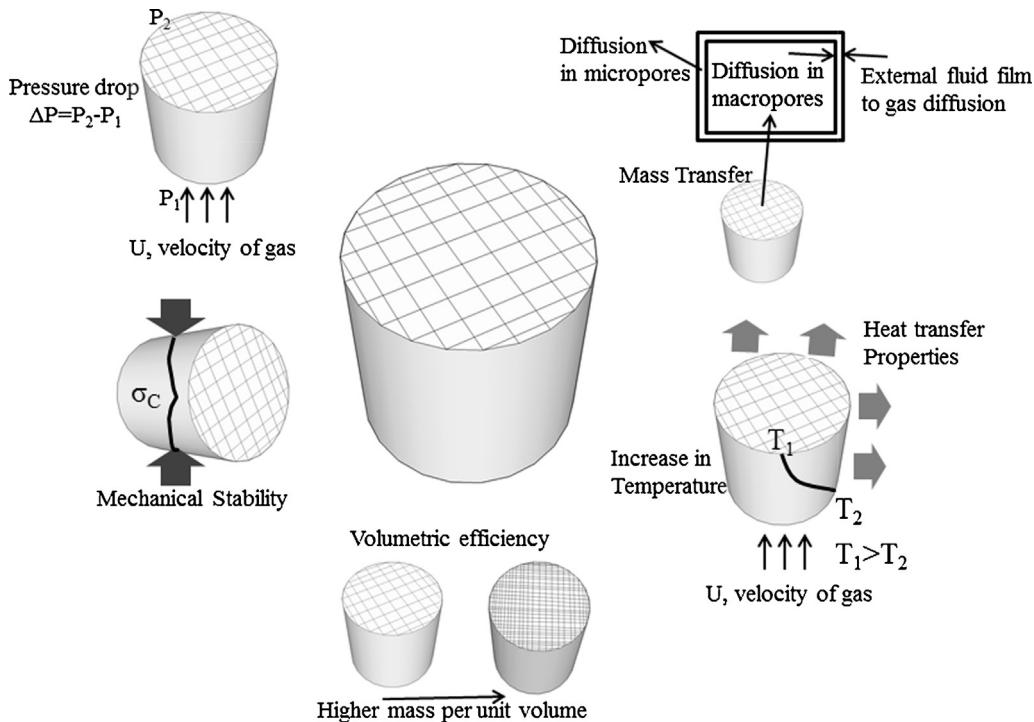


Fig. 3. Illustration of properties of structured porous adsorbents and catalysts; mass and heat transfer, gas diffusion kinetics, pressure drop, mechanical strength and volumetric efficiency, that are important for the separation and catalytic performance.

as guidelines for the design of high performance structured adsorbents and catalysts.

The transport of molecules through a porous material depends on the pore volume, pore size, chemical composition and the interactions between the molecules (normally in gaseous state) and the material.<sup>31</sup> In a structured adsorbent or catalyst, the mass transfer depends on the characteristics and diffusion length of the macropores, mesopores and/or micropores in the hierarchically porous structured material. All types of catalysts and adsorbents, irrespective of whether they are in the form of a packed bed of granules or consist of structured adsorbents and catalysts experience a pressure drop which needs to be minimized. The pressure drop across a packed bed can be given as<sup>176</sup>

$$\frac{\Delta P}{L} = 150 \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu}{R_p^2} U + 1.75 \frac{(1-\varepsilon)}{\varepsilon^3} \frac{\rho}{R_p} U^2 \quad (1)$$

where  $U$  is the superficial gas/mixture velocity,  $\rho$  is the density and  $\mu$  is the viscosity of the gas,  $R_p$  is the granule diameter and  $\varepsilon$  is the void fraction of the bed. Eq. (1) suggests that the adsorbents or catalyst should be structured with high void fraction ( $\varepsilon$ ) and large granule size ( $R_p$ ) to reduce the pressure drop. This is of course at odds with the need of small granule size for rapid diffusion and small void fraction for high volumetric efficiency.

Efficient removal of heat, or a careful matching of the mass and heat transfer kinetics from the adsorbent materials during the adsorption cycle is important in order to maintain the working capacity and selectivity of an adsorbent. This becomes especially complex in large installations, and several approaches such as the use of metals in the adsorption column or other heat transfer devices have been

suggested to facilitate the heat removal. This is often combined with appropriate design of the geometry of the adsorbent.<sup>177,178</sup>

Rezaei and Webley<sup>175</sup> defined throughput as a performance indicator of adsorbents. Throughput is directly connected to the working capacity, WC, of the adsorbent by the following relation:

$$\text{Throughput} = \frac{WC * \rho_B}{\tau} \quad (2)$$

where  $\rho_B$  is the adsorbent loading per unit volume and  $\tau$  is the cycle time. Working capacity is material specific and depends on the working temperature and pressure. Akhtar et al.<sup>73</sup> have defined a criterion called “figure of merit,  $F'$ ” to compare the performance of powder and structured adsorbents by taking into account the equilibrium selectivity and time dependent gas uptake. Mathematically, the figure of merit can be written as

$$F = \frac{f(S).N_{CO_2}}{\tau_{ads}} \quad (3)$$

where  $N_{CO_2}$  is the time-dependent capacity to adsorb CO<sub>2</sub>;  $\tau_{ads}$  is defined as the time for adsorption (capture); and  $f(S)$  is a function of the selectivity.

The design of structured adsorbents and catalysts involves inevitably a tradeoff between a number of parameters, which govern their overall performance. For example, a rapid mass transfer is obtained with granules of small radius<sup>175</sup> whereas this characteristic will result in a high pressure drop in a packed bed. High porosity enhances mass transfer and thus lowers the cycle time for adsorption whereas high loading of the catalysts or adsorbent per unit volume is required for a high throughput.

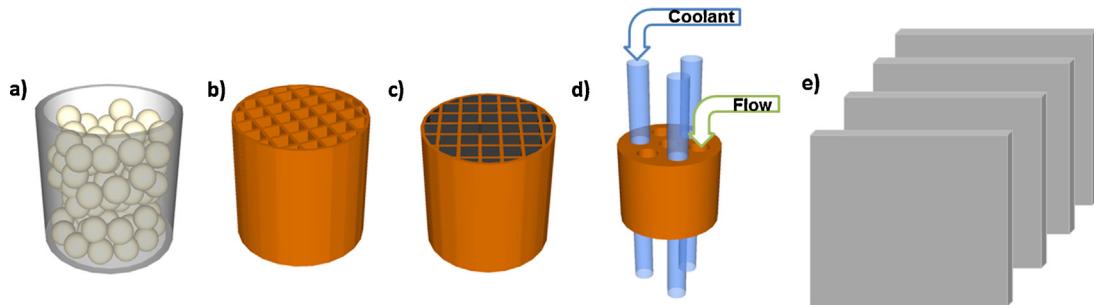


Fig. 4. Schematic examples of structured adsorbents: (a) beads; (b) honeycomb; (c) coated honeycomb; (d) monoliths with channels for flow of heat conducting media and mass transfer; and (e) laminates.

In practice, optimization depends on the requirements for the specific process and process conditions.

Recently, studies have shown that monoliths, honeycomb and other hierarchical structures (Fig. 4) offer advantages compared to conventional beads and granules in gas separation applications<sup>199–202</sup> and catalysis. Rezaei and Webley<sup>34,199</sup> showed that structured adsorbents with interconnected and branched macroporous channels are superior in performance to conventional adsorbents in the form of beads and granules. Kiwi-Minsker et al.<sup>203</sup> structured a catalytic wall micro-reactor designed as a thin cloth on an aluminum sheet and achieved three times lower pressure drop than the conventional packed bed reactors and also demonstrated a high catalytic performance for exothermic reactions. Zhu et al.<sup>204</sup> reported that decreased hydrophobicity and addition of mesoporosity to the traditional TS-1 zeolite greatly enhanced the catalytic performance in oxidizing thiophene in *n*-octane. Corning Inc. reported an extruded iron oxide honeycomb catalyst for the dehydrogenation of ethyl benzene to styrene with good performance over the standard radial-flow fixed-bed reactors.<sup>205</sup> Stuecker et al.<sup>206</sup> structured a fluid catalytic cracking catalyst consisting of rods, which had a high mass transfer, a low pressure drop, and a reported six times higher catalytic activity for the combustion of methane at 600 °C compared to extruded honeycombs. Examples of structured adsorbents emerging in gas separation are presented in Table 3.

#### 4. Structuring and processing of porous powders

Powder processing routes to produce structured adsorbents and catalysts have much in common with ceramic processing. The main processing steps involve: (i) mixing the porous powder with inorganic and organic additives, (ii) shaping the powders into the desired engineering shape, and (iii) removing temporal additives and creating a mechanically robust structure by thermal treatment. The porous powders are processed to produce structured bodies by a variety of shaping processes such as extrusion, slip and tape casting, foaming, gel casting, coating, spray drying, and dry pressing. The subsequent thermal treatment is primarily performed to increase the bonding in the shaped powder body but may be combined with a burn-out step for the removal of organic additives used to facilitate the shaping process. Inorganic binder such as clays and silica are commonly added to impart the desired mechanical strength.<sup>207–211</sup> In contrast, binder-less processing such as hydrothermal transformation<sup>212</sup> and pulsed current processing<sup>73</sup> minimizes the use of inactive binders while achieving high mechanical strength.

##### 4.1. Extrusion of pellets and honeycombs

Extrusion is a shaping process widely used to shape metals, polymers and ceramics in simple symmetrical shapes. Extrusion is probably the most widely used manufacturing method

Table 3  
Examples of structured adsorbents and applications.

Material	Structure	Application	Reference
Activated carbon	Monoliths	CO <sub>2</sub> separation, CH <sub>4</sub> storage, HC separation, Hg abatement	US8496734B2, <sup>179</sup> US20090295034A1, <sup>180</sup> US5658372A, <sup>181</sup> US 6258334B1 <sup>182</sup>
Activated carbon	Sheets, spiral wound, honeycomb	CO <sub>2</sub> separation	US7077891B2 <sup>183</sup>
Activated carbon	Cloth, fabric or felt,	H <sub>2</sub> separation	US8496734B2, <sup>179</sup> EP1342498A2, <sup>184</sup> US6565627B1 <sup>185</sup>
Activated carbon	Spiral roll or foams	Water purification	EP0402661B1, <sup>186</sup> US 20070155847A1 <sup>187</sup>
Zeolite	Monoliths	HC adsorber for exhaust, heavy metals, NO <sub>x</sub>	US 5582003A, <sup>188</sup> US8404026, <sup>189</sup> US7754638 <sup>190</sup>
Zeolites	Laminates, discs	Air separation	US20020170436 <sup>191</sup>
Zeolite	Hollow fibers, spiral wound, honeycombs	CO <sub>2</sub> separation	US8409332, <sup>192</sup> US 20120222554A1, <sup>193</sup> US 7959720 B2 <sup>194</sup>
MOFs	Monoliths, discs, sheets	Acidic gas separation, organic vapors, CO <sub>2</sub>	US 20120222555 A1, <sup>195</sup> US 20130047842A1, <sup>196</sup> US 20110297610A1, <sup>197</sup> EP 1812161A1 <sup>198</sup>

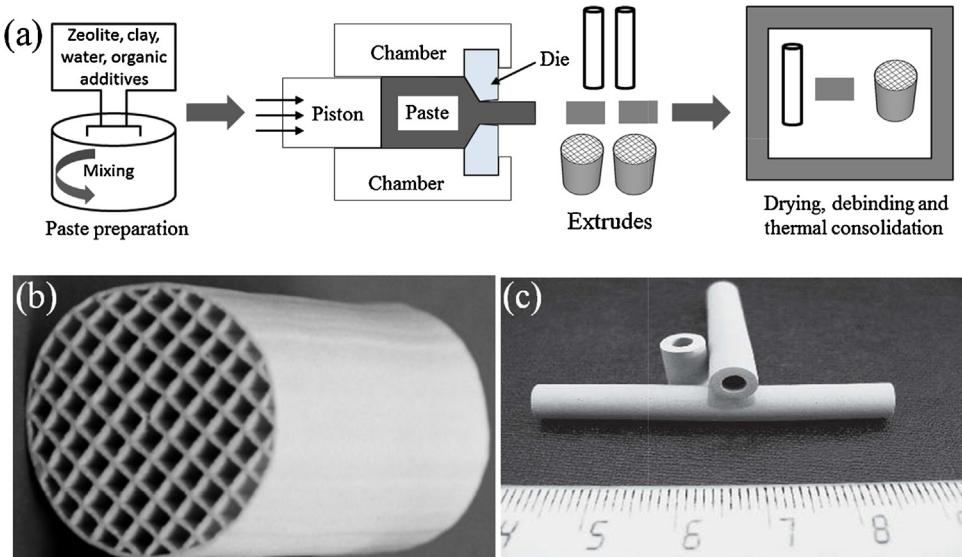


Fig. 5. Schematic diagram of the extrusion process and examples of extruded bodies: (a) overview of the extrusion and post extrusion processes; (b) image of a dried ZSM-5 honeycomb monolith, reprinted with permission from Aranzabal et al.,<sup>228</sup> © (2010) Elsevier; (c) extruded tubes of natural zeolites, reprinted with permission from Zacahua-Tlacuatl et al.<sup>213</sup> © (2010) Applied Rheology.

to structure and shape porous powders for adsorption and catalytic applications.<sup>56,57,190,207</sup> Extrusion has been established commercially to produce mechanically strong and attrition resistant granules, pellets and honeycomb structures of industrially important adsorbents and catalysts such as zeolite A, X, ZSM-5, MOFs and porous carbon for adsorption, air separation and catalytic applications. A schematic diagram of the extrusion process and examples of extruded bodies from ZSM-5<sup>213</sup> and natural zeolites<sup>214</sup> are presented in Fig. 5. Extruded honeycombs and tubes contain straight channels for rapid mass transport and microporous walls for the activity. Honeycomb structures provide a high geometric surface area to volume ratio, which results in high contact between the material and the flow stream. Honeycomb structures offer low pressure drop to the flow stream compared to conventional adsorption or catalytic beds. However, laminar flow through the honeycomb channels limits mixing of the gas stream and can thus lower the performance. Therefore, the geometrical parameters, e.g. wall thickness, cells per unit area and length of the honeycomb, are optimized to the process parameters e.g. flow rate of gas stream per unit volume, gas stream concentration, temperature and pressure for maximum capacity.<sup>215</sup>

The important processing operations in extrusion are; paste preparation, extruding the paste through the die, drying and thermal treatment. A kneading machine is usually employed to prepare a molding paste consisting of the porous powder, inorganic and organic additives and a solvent, commonly water. The molding paste must display suitable rheological properties, e.g. a significant plasticity, to allow the paste to be extruded through the die, and at the same time have sufficient cohesion to avoid formation of surface and bulk defects in the extruded product.<sup>108,204,216–219</sup>

The extrusion of porous adsorbents and catalysts usually requires the addition of inorganic particulate binders to make the

paste moldable and to impart the necessary mechanical strength in the green state and after thermal treatment. Commonly used binders are clays (aluminosilicates),<sup>108,220–222</sup> amorphous aluminophosphate,<sup>223</sup> alumina,<sup>224</sup> silica,<sup>225</sup> titania,<sup>226</sup> zirconia,<sup>226</sup> or a combination of two or more of these components.<sup>208</sup> Clay binders are popular as they make the paste plastic and at the same time impart a relatively high mechanical strength to the extruded bodies enabling handling and post treatment processes like cutting. Li et al.<sup>221</sup> found that an increase in the amount of bentonite binder increases the plasticity of the pastes and improves the possibility to extrude defect free zeolite bodies. It was found that more than 25 wt.% of bentonite was required to process crack-free honeycomb zeolite 5A structures after extrusion, drying and thermal treatment. Serrano et al.<sup>227</sup> found that the zeolite particle size and the zeolite to binder ratio in the paste had a significant effect on the mechanical properties of the extruded zeolite TS1 and that 40 wt.% inorganic binder content was required to impart the necessary strength for this catalytic application.

Various types of organic additives are added to the pastes to serve as thickening agents, lubricants, wetting agents, and temporary binders to improve the plasticity of the paste. Commonly used plasticizing agents for extrusion pastes are various types of modified water-soluble cellulose products, polyethylene glycol, polyvinyl alcohol, and glycerine.<sup>208,221,227</sup> Li et al.<sup>221</sup> reported that the addition of 1 wt.% hydroxyethyl-cellulose (HEC) to a paste containing zeolite 5A with 2 wt.% bentonite and 18 wt.% Hyplus 71 clay significantly reduced the size and number of defects in the extruded monoliths. Higher additions of HEC were reported to increase the flow resistance of the zeolite paste, resulting in problems with liquid migration under the very high extrusion pressure. Organic additives can also be added to increase the strength of the extruded bodies to minimize slumping or other shape changes. Zacahua-Tlacuatl<sup>213</sup> showed that an

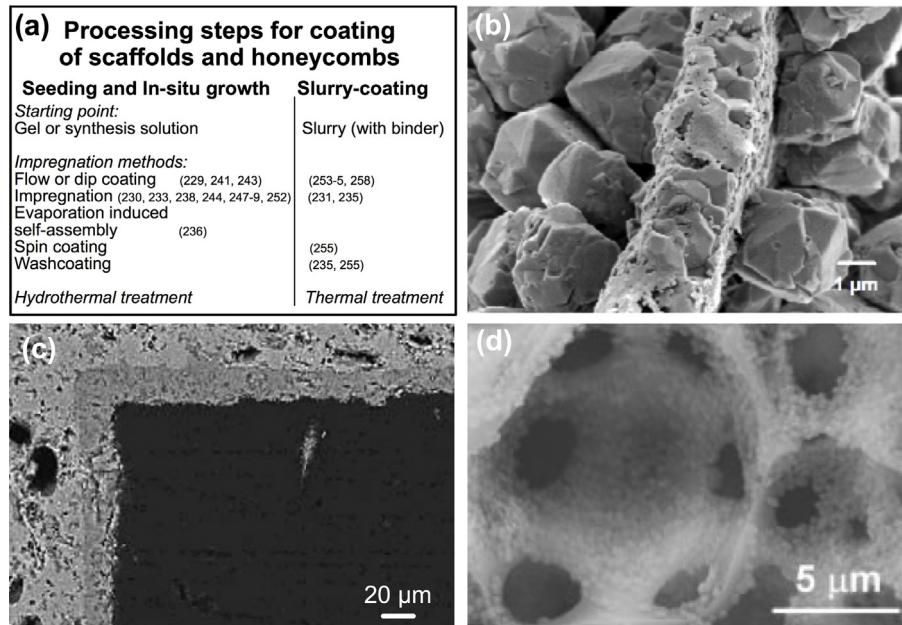


Fig. 6. Schematics of the processing steps for coating a macroporous structure and examples of monoliths with a foam-like structure coated with porous sorbents: (a) processing steps for coating of scaffolds and honeycombs; and (b) macroporous alumina coated with zeolite 13X via impregnation, reprinted with permission from Andersson et al.,<sup>231</sup> © (2012) Goeller Verlag GmbH, Germany. Note the good adhesion between the microporous zeolite powders and the dense alumina wall. (c) Cross-section view of a zeolite ZSM 5 film on a honeycomb monolithic support, reprinted with permission from Ulla et al.,<sup>243</sup> © (2003) Elsevier; and (d) SiOC cellular foam coated by in situ crystallization, reprinted with permission from Zampieri et al.,<sup>256</sup> © (2004) John Wiley and Sons.

addition of 1.5 wt.% of methylcellulose (MC) to a zeolite paste (61%, v/v) is necessary to maintain the shape of the extruded tubes. The criterion for selection of the correct additive and right proportion for extrusion process is complex and depends on the composition of the adsorbent/catalyst body, the design of the extruded objects and limitations in molding pressure.

#### 4.2. Coating of scaffolds and honeycombs

Coating of porous supports with active materials is an important method to produce structured adsorbents or catalysts that overcome mass and heat transfer limitations and high pressure drop associated with conventional packed beds of beads and pellets. Macroporous monoliths in the form of honeycombs and foams can act as supports for coating of micro- and mesoporous particulate adsorbents and catalysts. The support provides the desirable mechanical stability together with an efficient mass and heat transfer and low pressure drop.<sup>175,214</sup> Several methods of coating porous scaffolds and honeycombs are in practice. Details of types of substrates and coating techniques are discussed in the following sections and illustrated in Fig. 6.

Honeycomb materials are traditionally used in automobile industry as supports of catalytically active materials. They have a high strength-to-weight ratio, low pressure drop for gas applications and are manufactured in a variety of materials and with a wide range of cell densities. Honeycombs used for coatings of porous adsorbents have cell densities typically between 400 and 1200 cells per square inch. Biological specimens can show pore morphologies similar to those of honeycombs. Li et al.<sup>229</sup> used biomorphic honeycomb monoliths produced from

cuttlebone as substrates for thin films of silicalite-1 and NaX zeolite. The cuttlebone honeycombs have an exceptionally high cell density of 16,000 cells per square inch. Onyestýák et al.<sup>230</sup> studied pyrolyzed wood as carbon-based supports for thin films of zeolite NaX. The carbon surface was treated to reduce its hydrophobic character and enabled impregnation with water based dispersions and solutions.

Other types of macroporous supports for gas separation applications include open cell ceramic foams<sup>231,232</sup> or foam-like materials.<sup>233</sup> Coating on ceramic foams results in composite materials with relatively high mechanical strength, low pressure drop<sup>214,234</sup> and high accessibility to the active adsorption sites in the porous particulate coating.<sup>235</sup> It may however be challenging to achieve homogenous coatings of particulate adsorbents on irregular foam structures compared to the highly organized honeycombs.

Low-cost alumina-based ceramics, such as cordierite,<sup>81,236–243</sup> aluminosilicate<sup>231</sup> and alumina,<sup>231,244</sup> are important supports for catalysts and adsorbents. Cordierite has traditionally been the material of choice for high temperature applications due to its low thermal coefficient of expansion and thus excellent thermal shock resistance. However, Ulla et al.<sup>243</sup> showed that an Al-rich support, such as cordierite, may hinder the formation of crystalline zeolite coatings of a high Al content. Other interesting support materials are different types of ceramics<sup>233,244</sup> and carbon-based materials.<sup>230</sup> Porous metallic supports are available for exhaust application. Pace et al.<sup>245</sup> reported a corrugated metal substrate consisting of flat and corrugated foils for particulate filtration. The flat metallic foil layer is a porous fleece that can be coated with a catalyst for exhaust gas and particulate remediation. Such catalyst can e.g. be NO<sub>x</sub> adsorbers or

zeolites. Porous metallic foams such as Ni-based alloy foams have also been coated and successfully used in a cross-flow design to remove diesel exhaust particulates and for gas treatment.<sup>246</sup>

Coating of the macroporous support is commonly performed using a two-step process that can e.g. include slurry-coating, in situ growth or seeding followed by heat treatment. The heat treatment is aimed at generating strong bonding or adhesion between the active particulates and the support surface, either through a sintering process or in situ growth of the porous material. Thermal treatment is however not always necessary. Wan et al.<sup>236</sup> showed that ordered mesoporous coatings of carbon can be achieved directly on honeycomb cordierite substrates using a structure directing agent during evaporation induced self-assembly. The coated support could be used for more than 200 repeated cycles without any obvious loss in either adsorption capacity or mass.

Seeding and in situ growth of porous materials, e.g. zeolites, on macroporous sacrificial templates, such as polymer foams<sup>247,248</sup> and biological specimens<sup>249,250</sup> can result in hierarchically porous materials. Seeding and in situ growth has been achieved by impregnating the support with a gel or synthesis solution,<sup>230,238,244</sup> flow coating or dip coating<sup>229,241,243</sup> and evaporation induced self-assembly,<sup>251</sup> followed by a hydrothermal treatment to trigger in situ growth. These methods are associated with long processing times but achieve stronger adhesion between the porous coating and the support compared to particulate coating processes. Mosca et al.<sup>238</sup> designed adsorbent materials with a low pressure drop and high adsorption capacity of CO<sub>2</sub> by coating cordierite honeycombs with micron-thick NaX zeolite layers using a seeding technique followed by hydrothermal treatment. Rezaei et al.<sup>252</sup> studied the effect of the zeolite film thickness on the performance of coated cordierite monoliths and found through simulations that for CO<sub>2</sub> adsorption a 10 µm thick zeolite X film is optimal for a non-porous 1200 cpsi monolith. Micro- and mesoporous films can also be produced onto macroporous supports by slurry-coating,<sup>235,238</sup> dip coating<sup>253–255</sup> and impregnation,<sup>231,235</sup> chemical or physical vapour deposition<sup>251</sup> or by the use of preceramic polymers<sup>256</sup>. The volume fraction of the active porous material is usually lower in these types of composite materials compared to coated honeycombs. Compared to in situ growth of zeolites, zeolite films deposited by slurry coating also contain meso and macroporosity which provides higher accessibility to the active adsorption sites.<sup>235,253,257</sup> Mitsuma et al.<sup>258</sup> produced a honeycomb laminate by coating a ceramic fiber paper of high thermal stability with a high silica zeolite through dip coating. Zamaro et al.<sup>240</sup> studied the effect of slurry viscosity and volatility of different slurry solvents on the thickness of ZSM-5 zeolite coatings deposited on cordierite honeycomb substrates and found that the highest zeolite loading was achieved for slurries with both high viscosity and volatility. Recently, Shekhah et al.<sup>259</sup> reported the successful growth of metal organic framework thin films on silica foam by stepwise layer-by-layer (LBL) growth.

Silva et al.<sup>235</sup> showed that by treating the surface of cordierite foam with a cationic polymer, the ZSM-5 zeolite loading could

Table 4

Isoelectric point and Hamaker constant in vacuum of microporous materials.

Material	Isoelectric point (pH)	Hamaker constant (J) <sup>a</sup>
Silica (quartz)	2	$8.9 \times 10^{-20}$
Alumina	9	$15.2 \times 10^{-20}$
Zeolite 13X	4.7 <sup>153</sup>	$8.7 \times 10^{-20}$
Zeolite 4A	7.0 <sup>201</sup>	$7.7 \times 10^{-20}$
Silicalite-1	5.8 <sup>203</sup>	$7.9 \times 10^{-20}$
Activated Carbon	5.4 <sup>204</sup>	$6.0 \times 10^{-20}$

<sup>a</sup>Bergström<sup>273</sup> and Akgun et al.<sup>274,275</sup>

be increased by 100 wt.%, compared to a non-surface treated foam surface. Fig. 6b illustrated how homogenous and dense coatings of zeolite 13X could be produced by optimizing the pH of the colloidal zeolite 13X suspension to maximize the electrostatic attraction with the alumina foam support, which had been pretreated with a cationic polyelectrolyte.<sup>231</sup> The CO<sub>2</sub>-uptake of the coated ceramic foam was as high as 5 mmol CO<sub>2</sub> per gram zeolite 13X, which is close to the capture performance of binder-less hierarchically porous zeolite 13X monoliths (6 mmol CO<sub>2</sub>/g zeolite 13X).<sup>169</sup>

#### 4.3. Colloidal processing and casting of porous powders

Colloidal processing offers methods of shaping macroscopic monoliths and powder bodies on an industrial scale. The commonly used colloidal shaping methods are tape casting, slip casting, gel casting and perhaps powder injection molding. Applying colloidal processing methods to shape porous powders into structured adsorbents and catalysts is always based on dispersing the porous particles in a liquid or polymer with dispersant, binder, plasticizers and antifoaming agents<sup>260</sup> and mixing and deagglomerating using e.g. ball milling or high shear mixing. The colloidal and rheological properties of the suspensions must be optimized for the particular forming process. Injection molding uses e.g. highly concentrated suspensions that are highly plastic and possess a yield stress while slip casting is normally performed using Newtonian suspensions with an intermediate solids loading. The interparticle forces between the powder particles control the colloidal and rheological behavior of the suspension, e.g. repulsive forces between the powder particles result in a homogeneously dispersed fluid suspension and attractive forces can result in an agglomerated viscous suspension displaying a significant yield stress.<sup>261,262</sup>

The dominating interparticle forces in particle suspensions are van der Waal's, electrostatic and steric forces. The van der Waal forces are electrodynamic in origin and result from the interaction between the oscillating or rotating dipoles in the interacting media.<sup>263</sup> The magnitude of van der Waals interactions of solid materials with other solids or fluids can be estimated from the materials dependent Hamaker constant. Table 4 shows that the Hamaker constant in vacuum for the porous zeolites is around 80 zJ which is similar in magnitude to silica but significantly smaller than for alumina. The ubiquitous van der Waals interactions are usually attractive and will result in uncontrolled aggregation of the

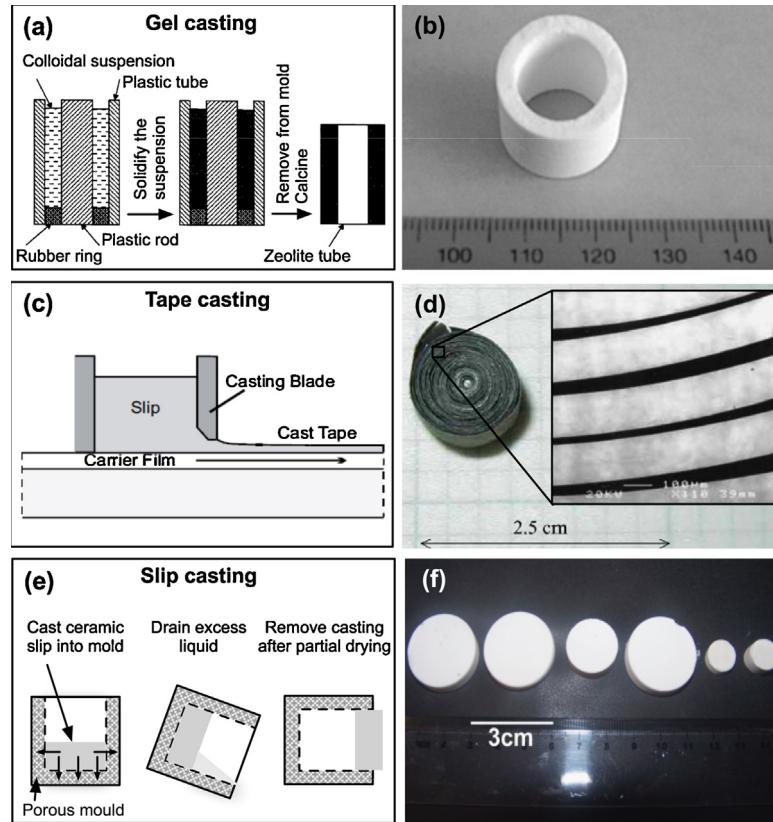


Fig. 7. Schematic of important casting processes (a, c, e) together with examples of cast parts; (b) gel-cast silicalite-1 tube, reprinted with permission from Wang et al.,<sup>276</sup> © (2001) The Royal Society of Chemistry; (d) tape cast microchannel catalyst, reprinted with permission from Bae et al.,<sup>281</sup> © (2005) Elsevier; and (f) slip cast green bodies of zeolite 13X, reprinted with permission from Akhtar et al.,<sup>169</sup> © (2011) John Wiley and Sons.

dispersed particles unless they are balanced by interparticle repulsive forces. Repulsive interparticle forces can be induced from the electrostatic double layer generated by the charge at the solid–liquid interface or the increase in mixing entropy when adsorbed polymer layers overlap.<sup>260–262</sup> The DLVO (Derjaguin–Landau–Verwey–Overbeek) theory<sup>264</sup> gives an accurate description of the colloidal interactions between charged particles. The charge on the particle surfaces are often pH-dependent and can be related to the isoelectric point and the electric potential at the shear plane estimated from electrophoretic mobility measurements ( $\zeta$ -potential). Electrophoretic mobility measurements on porous powders are usually performed as a function of pH and ionic strengths.<sup>265–272</sup> The isoelectric points (IEP) for some selected zeolites and other inorganic materials are shown in Table 4.

Rheology measurement provides information on the flow and viscoelastic properties of the concentrated suspensions and is an important processing parameter for colloidal processing.<sup>219,260–262</sup> The rheological response of the colloidal suspensions originates from the interplay of the thermodynamic and fluid mechanical interactions and depends e.g. on the particle concentration and the nature and magnitude of interparticle forces. Typically, the colloidal shaping routes require preparation of stable particle suspensions.

The versatility and simplicity of the colloidal forming techniques have been used for shaping of porous powders into a variety of structures.<sup>276–278</sup> Gel-casting was recently used

to shape zeolite powders into hierarchically porous tubes (Fig. 7b).<sup>276</sup> Silicalite-1 tubes have been gel cast by dispersing nanocrystals with a solid loading of 30–40 wt.% in an aqueous solution with the monomer acrylamide, crosslinker *N,N'*-methylenebisacrylamide, and initiator ammonium persulfate and crosslinking the solution by heating the suspension at 50 °C in a tubular mold.

Vasconcelos et al.<sup>279</sup> prepared diatomite-based membrane filters with a well-defined pore-size and porosity by slip casting or tape casting stable suspensions of 50 wt.% diatomite together with starch as a sacrificial pore former. Functionally graded bodies of dense, ceramic and porous powders have recently been prepared by a hybrid colloidal processing process comprising slip casting and electrophoretic deposition.<sup>280</sup> Bae et al.<sup>281</sup> prepared a micro-channel catalyst suitable for hydrogen-reforming of natural gas and gasoline by tape casting (Fig. 7d). The tape-cast micro-channel catalyst showed an enhanced mass transport and a five-fold increase in the catalytic performance compared to packed beds. Monoliths of zeolite 13X have been prepared<sup>169</sup> by slip casting of an electrostatically stabilized suspension at alkaline pH (Fig. 7f). The slip cast and thermally consolidated zeolite 13X monoliths displayed good mechanical strength (0.7 MPa) and high CO<sub>2</sub> adsorption capacity (6 mmol CO<sub>2</sub> per gram at 273 K). Akhtar et al.<sup>272</sup> also produced hierarchically porous zeolite monoliths with spherical and rod-like pores by colloidal processing of the zeolite powders together with a sacrificial template material (carbon fibers and glassy carbon spheres).

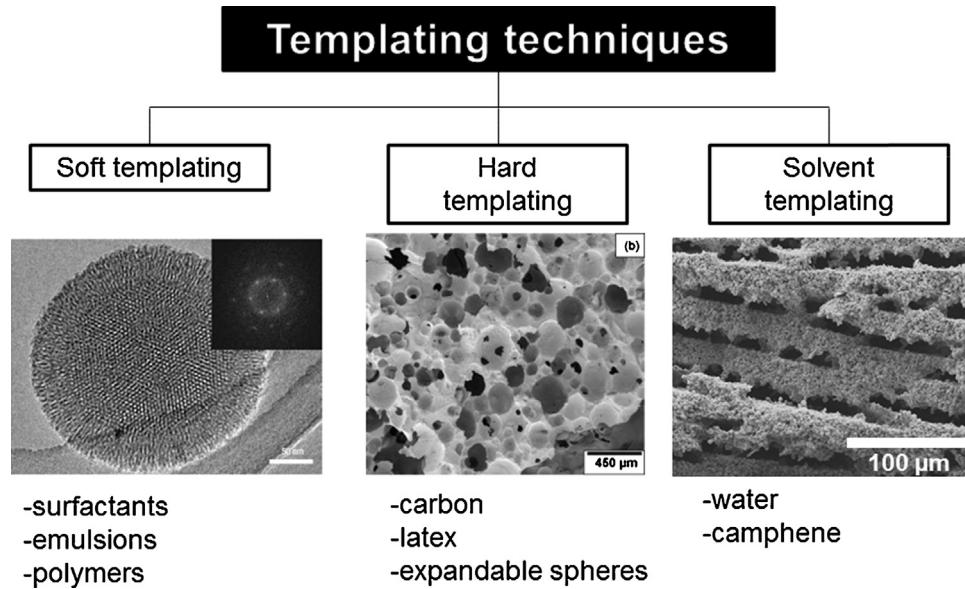


Fig. 8. Examples of various templating techniques used to produce structured adsorbents and catalysts (soft templating, reprinted with permission from Che et al.,<sup>292</sup> © (2003) Nature publishing group. Hard templating, reprinted with permission from Andersson et al.,<sup>293</sup> © (2008) Elsevier. Solvent templating, reprinted with permission from Ojuva et al.,<sup>294</sup> © (2013) American Chemical Society.

#### 4.4. Sacrificial templating

Templating strategies are commonly employed to create porosity on all length scales. Soft templating approaches (Fig. 8) utilize e.g. polymers,<sup>282,283</sup> surfactants,<sup>284</sup> emulsions,<sup>285</sup> carbon,<sup>286</sup> foaming agents,<sup>287</sup> liquid crystals,<sup>288</sup> and sponges<sup>289</sup> to produce macroporous materials. Hard-templating or nanocasting (Fig. 8) produces porous nanostructures by impregnating preformed templates with precursor liquids or solutions. On subsequent solidification and removal of the template, a porous nanostructure is obtained with a negative replica of the template.<sup>290</sup> Several studies have extended the application of nanocasting to design hierarchically porous materials by impregnation of a hard template with colloidal suspensions of porous particles, e.g. zeolites.<sup>277,291</sup> Hollow zeolite spheres have been produced by coating polystyrene spheres by nanozeolite particles using a layer-by-layer technique followed by removal of the polystyrene core by thermal treatment at 600 °C.<sup>277</sup> Zhang et al.<sup>291</sup> fabricated ordered macroporous zeolite fibers prepared by the infiltration of swollen bacterial supercellular threads with silicalite-1 nanoparticles.

Another versatile templating method is solvent templating (Fig. 8) where the main technique is freeze casting.<sup>295</sup> Freeze-casting is an approach for shaping powders in highly porous and highly anisotropic structures. Controlled freezing of a suspension results in formation of segregated ice crystals and dense particle rich domains. Ice is sublimated to achieve a green body containing residual ice-templated pores. The green body is then subjected to a thermal treatment cycle to consolidate the solid walls. Freeze-casting produces monoliths with open porosity in the range of 20–80 vol.%<sup>295</sup> and with pore dimensions in the range of 2–200 μm.<sup>296</sup> The pore morphology depends largely on the solidification characteristics of the solvent, additives and freezing conditions.<sup>295</sup> Ojuva et al.<sup>294</sup> showed how

laminated adsorbents with different pore sizes and wall thicknesses could be structured by freeze-casting of aqueous suspensions of zeolite 13X and a clay binder (Fig. 9). The freeze-cast and thermally treated laminated adsorbents showed a very high initial CO<sub>2</sub> uptake, and high adsorption capacity. Mori et al.<sup>297</sup> demonstrated how freeze-casting of a silica gel into a honeycomb structure followed by converting the silica gel by steam resulted in silicalite-1 monoliths with a hierarchical porous structure with channel diameters of 10–50 μm.

#### 5. Producing mechanically strong structured adsorbents and catalysts using inorganic binders and binder-less approaches

Structured adsorbents and catalysts usually require an inorganic binder to provide the mechanical stability needed to withstand the stress during operation.<sup>208</sup> Commonly used binders for porous sorbents can be divided into inorganic and organic binders. The inorganic binders typically used are aluminosilicates, amorphous aluminophosphate, alumina, silica, titania, zirconia, clays or a combination of two or more of these components.<sup>208,298</sup> The practice, illustrated in Fig. 10, is to subject the powder body containing a mixture of the active porous powder, e.g. a zeolite, and the non-porous inorganic binder, e.g. a clay to an elevated temperature to induce strong bonds between the particles.<sup>108,209,220–222</sup> Macroscopic porous adsorbents are also processed with permanent organic binders, particularly when the adsorbents are used for low-temperature applications like removal of moisture and for the adsorption of volatile organic components from air.<sup>210</sup> Cecchini et al.<sup>211</sup> reported how a paper making technique could be used to prepare sheets of zeolite paper containing ceramic or cellulose fibers that exhibited a high mechanical stability and good adsorption capacity for toluene.

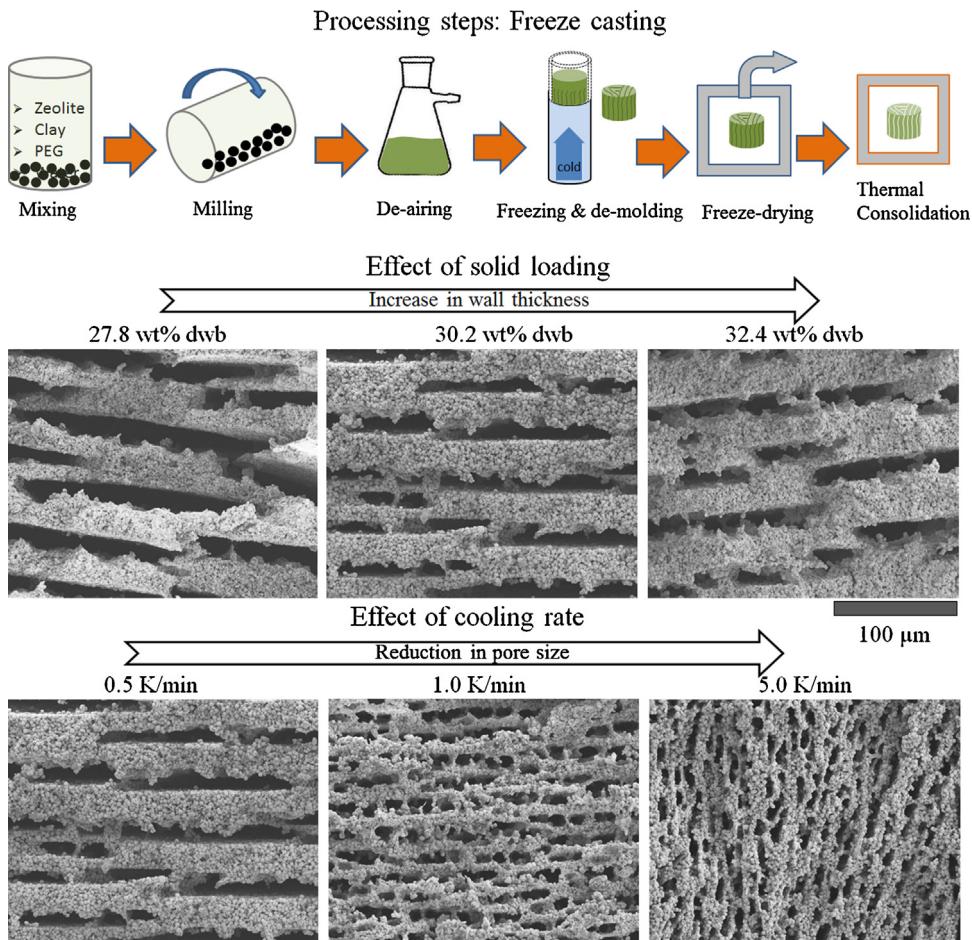


Fig. 9. Schematic diagram of the freeze-casting process. The microstructures show the effect of solid loading and cooling rate on the wall thickness and pore size, respectively.

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Kaolin, attapulgite, sepiolite and bentonite clays are commonly used binders for zeolites.<sup>220,299–301</sup> The calcination temperature of a zeolite-binder structured body is always lower than the thermal stability of the zeolite. The temperature and binder is selected to achieve a mechanically strong body while keeping the surface area of zeolites intact (Fig. 10). The thermally induced increase in strength is probably related to the creation of new and stronger bonds both between the binder phase and the porous powders and between the porous powders themselves. Recent work has shown that it is possible to visualize local binder interactions with zeolite crystals by micro tomography (micro-CT), synchrotron radiation X-ray tomographic microscopy (SRTXM) and FIB-SEM in combination with EDX.<sup>89</sup>

The thermal stability of zeolites depends on the Si/Al ratio, the framework type, and the extra framework cations. Zeolites with Si/Al larger than 4 are frequently stable above 800 °C while zeolites with Si/Al ratio lower than 4 are only stable at lower temperatures.<sup>302</sup> The pure silica analogs of zeolites are thermally stable to very high temperatures, e.g. up to 1300 °C for silicalite-1.<sup>303</sup> The geometry of the framework undoubtedly influences the thermal stability of zeolites. It has been reported that zeolites with high framework density, only slightly distorted or twisted

rings (T–O–T angles) and with five membered rings have high thermal stability.<sup>304,305</sup> Furthermore, zeolites containing monovalent charge compensating cations are more thermally stable compared to zeolites containing divalent cations; the thermal stability of chabazite e.g. increases through the alkali series from Li to Rb from 731 °C to 1100 °C.<sup>306</sup> Zeolitic imidazole frameworks (ZIFs) like most metal organic frameworks has a significantly lower thermal stability than zeolites. The crystalline framework of ZIFs collapse at temperatures above 350 °C.<sup>307</sup> However, recent work of Gustafsson et al.<sup>308</sup> have reported a family of homeotypic porous lanthanide metal organic frameworks with high thermal stability up to 600 °C. The thermal stability of a number of important porous solids is presented in Table 5.

Depending on the capacity for ion exchange, it is also necessary to control the addition of other structuring aids and avoid high alkalis or alkali earth metals sources. This addition could potentially result in ion-exchange when water is eventually added to knead and shape the powder mixture and possibly result in a reduced performance. However, some binders can improve the properties to the active, porous material. Kim et al.<sup>314</sup> reported e.g. that an alumina binder increases the operating temperature for zeolite Na-ZSM-5 used for the conversion of crude methanol to dimethyl ether. It is also important to optimize the

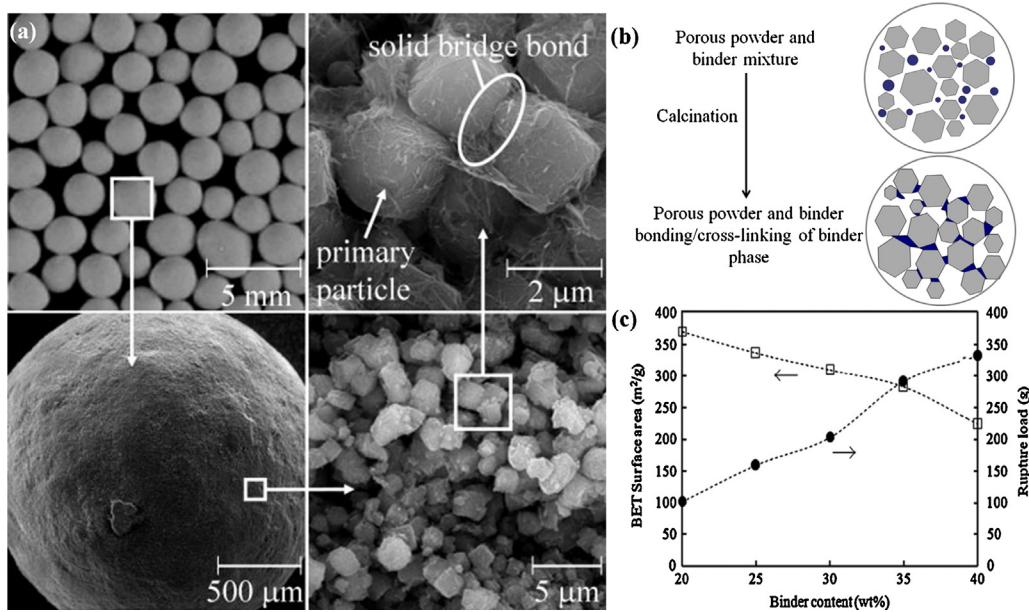


Fig. 10. Binder-assisted bonding of microporous powders: (a) illustration of the binder-assisted bonding of microporous powder, reprinted with permission from Müller et al.,<sup>317</sup> © (2012) John Wiley and Sons. Magnified SEM images show that the granule microstructure consists of zeolite particles bonded by clay binder; (b) schematic of bonding process of porous particles and inorganic binder; (c) the effect of bentonite binder on the BET surface area and rupture load of the fabricated granules of zeolite Y, reprinted with permission from Charkhi et al.,<sup>209</sup> © (2012) Elsevier.

mass and heat transfer properties of the binder-containing structured adsorbent or catalyst. The chemical durability of the binder may be lower than the durability of the porous powder which can result in a loss of strength and variation of mass transfer and mechanical properties with time as the binder wears down.<sup>315</sup>

Binder assisted macroscopic metal organic framework (MOFs) bodies have been produced by pressing, extrusion, foaming and spray granulation.<sup>198,316</sup> Binders that infer a mechanical strength of particulate MOF bodies include hydrated alumina, silicon compounds, clays, alkoxysilanes and graphite, cellulose, starch, polyacrylates, polymethacrylates and polyisobutane. The shaped MOFs are usually thermally treated below 300 °C to ensure that the framework integrity is retained.

Although the binders impart mechanical strength and attrition resistance, the incorporation of inactive binder dilutes the active component, i.e. the porous powder, which results in a reduced performance per unit mass (or volume) of the

structured adsorbent or catalyst. Furthermore, the binder can cover the surface of the adsorbent or catalyst powder and cause pore blockage. Hence, the desire to produce high surface area adsorbents and catalysts with high capacity and high volumetric efficiency has triggered the development of binderless processing approaches.<sup>318</sup> Binder-less processing primarily relates to hydrothermal transformation of the binder/non-zeolitic material to zeolites, and pulsed current processing of porous powders to produce mechanically strong, hierarchically porous macroscopic bodies without any addition of inorganic binders.

The hydrothermal transformation route uses a starting material, e.g. clay or silica, which can be transformed into the desired microporous material without affecting the macroscopic shape of the structured material. Pavlov et al.<sup>319</sup> have recently reviewed the literature on the hydrothermal transformation of clay binder to produce binderless granules of zeolite NaX and zeolite NaA. Production of binder-less zeolite granules or pellets by hydrothermal transformation of clay, e.g. kaolin, has limitations. The impurities present in the clay e.g. make it difficult to achieve a crystallinity of the produced zeolite phase exceeding 80%.<sup>212,320</sup> The crystallinity can be increased by seeding<sup>321</sup> or by using very pure porous glass beads as a starting material.<sup>322</sup> Scheffler el al.<sup>323</sup> showed how glass beads ( $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ) could be hydrothermally transformed into MFI-type zeolite beads in an aqueous mixture of an aluminum source and terapropylammonium bromide at 175 °C.

Recently it was demonstrated how binder-free, mechanically strong monoliths could be directly produced using various types of porous powders by Pulsed Current Processing (PCP).<sup>73,303,309,324</sup> The PCP process provides the advantage of

Table 5  
Thermal stability of industrially important microporous materials.

Porous material	Thermal stability (°C)	Reference
Zeolite NaX	800	Akhtar et al. <sup>169</sup>
Zeolite NaA	750	Akhtar et al. <sup>73</sup>
Silicalite-1	1300	Akhtar et al. <sup>303</sup>
ZSM-5	1100	Vasiliev et al. <sup>309</sup>
ZIF62	350	Gustafsson et al. <sup>307</sup>
Er-MOF	550	Gustafsson et al. <sup>308</sup>
NaY	882	Trigueiro et al. <sup>310</sup>
CHA-Na	800	Cruciani et al. <sup>302</sup>
SAPO-34	1000	Wondraczek et al. <sup>311</sup>
MOF-[Sr(DMF)-(μ-BDC)]	500	Pan et al. <sup>312</sup>
MOF-Cu <sub>3</sub> (BTP) <sub>2</sub>	450	Colombo et al. <sup>313</sup>

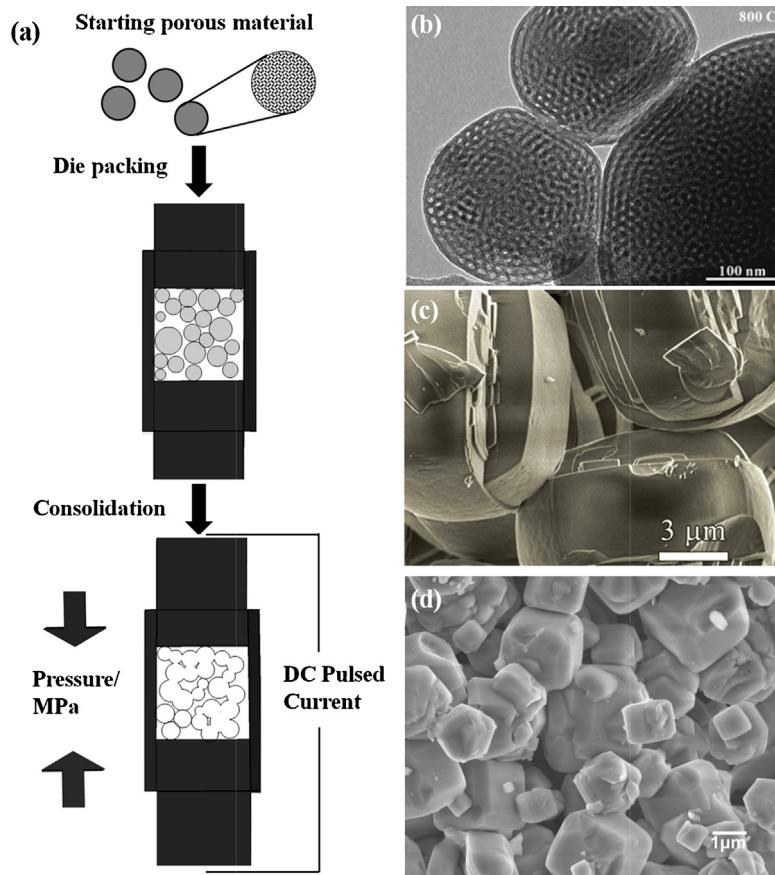


Fig. 11. Binder-less processing of porous powders using pulsed current processing: (a) schematic illustration of the pulsed current processing to prepare porous monoliths from porous adsorbent material; (b) TEM image of the deformed contact zone of the P123-templated, polydisperse mesoporous silica particles, subjected to 20 MPa applied pressure and rapid heating to 800 °C, reprinted with permission from Vasiliev et al.,<sup>324</sup> © (2006) American Chemical Society; (c) SEM micrograph of zeolite silicalite-1 monoliths (PCP-treated at 1100 °C), reprinted with permission from Vasiliev et al.,<sup>309</sup> © (2010) American Chemical Society; and (d) SEM micrograph of PCP-treated zeolite 4A monolith at 600 °C, reprinted with permission from Akhtar et al. 73, © (2012) The Royal Society of Chemistry.

high heating rates which makes it possible to partially fuse the porous particles together with a minor loss of the intrinsic surface area. PCP has been used to produce mechanically stable hierarchically porous monoliths from macroporous,<sup>325</sup> mesoporous<sup>324</sup> and microporous<sup>73,303,309</sup> powders (Fig. 11). The binder-free PCP production route requires that the temperature (and pressure) range where the mass transport is insignificant and the characteristic porosity of the starting powders is preserved is identified. The binder-less PCP process has been used to produce silicalite-1 membrane supports with a high mechanical strength (10 MPa) and high permeability for gases like H<sub>2</sub>, He, N<sub>2</sub>, and CO<sub>2</sub>.<sup>303</sup> Interestingly and of high relevance for the production of crack-free all-zeolite membranes, the binder-less membrane support showed a negative coefficient of thermal expansion similar to the silicalite-1 crystals and films. Akhtar et al. showed recently that PCP consolidated partially K<sup>+</sup> exchanged zeolite NaA monoliths with a high mechanical stability of 2 MPa display a high CO<sub>2</sub> uptake capacity and outstanding selectivity 73. The hierarchically porous monoliths show a rapid uptake and the low-cost PCP consolidated binder-less and mechanically strong monoliths of zeolite NaKA compared favorably with porous carbon and MOF materials.

## 6. Summary and outlook

Hierarchically porous structured adsorbents and catalysts have the potential to overcome the shortcomings of conventional packed beds of beads or granules. High pressure drop, poor mass and heat transfer, low mechanical and attrition resistance are a few examples of these shortcomings. In addition, structured adsorbents and catalysts provide the freedom to tune the properties relevant to their performance by controlling the hierarchically porous structure. Fig. 12 gives an overview of the state of the art processes to structure porous powders into adsorbents and catalysts for important applications together with the important geometrical characteristics that control pressure drop, mass and heat transfer, and mechanical integrity.

We have summarized important findings from the open literature and patents on structuring of commercially important porous adsorbents and catalysts ranging from well-established techniques like extrusion and coating of scaffolds to more recently introduced processing methods like direct casting and sacrificial templating. We have identified and described binder-assisted and binder-free approaches for shaping porous powders into mechanically strong monoliths. It is shown that the selection of a binder phase with functionalities relevant to the

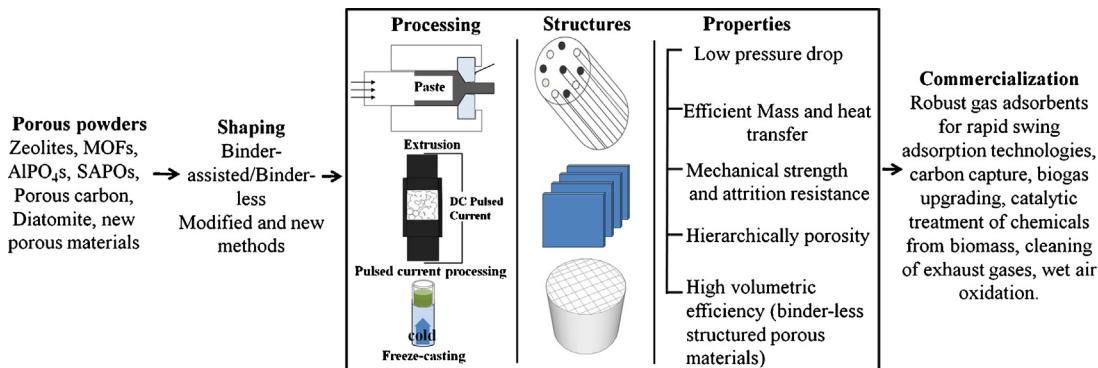


Fig. 12. Shaping of porous powders into robust adsorbents and catalysts.

application can enhance properties of the structured materials e.g. mechanical strength. Recently developed binder-less structured materials have advantages over binder-assisted structured materials in terms of volume efficiency and performance. Binder-less processes using hydrothermal conversion of inorganic clay to porous material are however limited to only a few clay–zeolite systems. The recently developed pulsed current processing route to directly shape porous powders into mechanically strong structured bodies without addition of binders is described in detail. This promising technique can be developed further and possibly be combined with 3D printing techniques to extend the range of porous materials, and hierarchically porous architectures. With the development of more volume efficient adsorbents and catalysts, there is a need to improve the heat transfer properties. This challenge could be met by designing structured adsorbents and catalysts with additional cooling channels or by introducing materials with a high heat transfer, e.g. carbon, in the structured materials.

The production of high performance structured adsorbents and catalysts will require further development of efficient and facile routes to structure porous powders into complex shaped, hierarchically porous materials. Rapidly growing applications in very large-scale processes such as carbon capture and production of chemicals from biomass will require a close collaboration between materials scientist, chemists and chemical engineers to meet challenges related to e.g. energy efficiency and yield.

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