Production of spherical molecularly imprinted polymeric particles containing CO2-philic nanocavities

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In this study, we have developed novel spherical molecularly imprinted polymeric particles containing amine-decorated nanocavities for CO₂ capture, called CO₂-MIPs, using suspension polymerization (Fig. 1). The key parameters for high affinity of CO₂-MIPs towards CO₂ molecules are (a) tuned chemical architecture of the nanocavities, and (b) the presence of amine functional groups, which are covalently incorporated within the nanocavities. Previously, it was shown that CO₂-MIPs produced by bulk polymerization have a high CO₂ selectivity (separation factor up to 340) and stable capture capacity in the presence of moisture and impurities, such as SO₂, NO, and O₂ [1, 2]. However, the bulk polymerization includes crushing, grinding and sieving steps, which are time-consuming and wasteful, because only 30-40% of particles can be recovered. In addition, the produced particles have irregular shapes and sizes and can undergo mechanical attrition and break down to finer particles during the CO₂ capture process. Moreover, the bulk polymerization process is hardly scalable. On the other hand, suspension polymerization is an established method for industrial-scale production of polymeric particles in which each individual monomer drop acts as a tiny batch reactor, leading to an increase in the heat transfer and faster polymerization.

The size of the particles was 70-210 µm, depending on the agitation speed in the jacketed reactor. The nitrogen adsorption-desorption analysis showed Type IV isotherm, implying the uniform pore size distribution. The specific surface area and pore volume of the particles were up to 457 m²/g and 0.92 cm³/g respectively. The thermogravimetric analysis revealed that the particles were thermally stable up to 220°C. By comparing CO₂ breakthrough curves of imprinted polymer (CO₂-MIPs) and non-imprinted polymer (NIPs) particles, it was found that the presence of nanocavities resulted in a higher CO₂ capture capacity (Fig. 1c). In addition, increasing the NH₂ density caused higher CO₂ uptake.

![Figure 1. (a) A conceptual scheme of CO₂-MIPs synthesize process: (i) Monomer-template self-assembly, (II) Crosslinking of monomer-template complex, (III) Template removal, (IV) CO₂ capture, (V) CO₂ released; (b) SEM image of produced particles; (c) Comparison of CO₂ capture capacity of MIPs and NIPs. Acrylamide was used as a monomer,](image-url)