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Review

Critical review of existing nanomaterial adsorbents to capture carbon dioxide and methane

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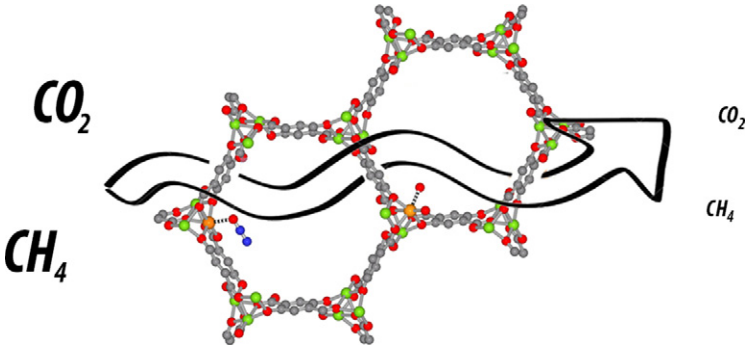
HIGHLIGHTS

- Novel materials and nanomaterials for CO_2 and CH_4 sorption are presented and compared.
- These materials have high selectivity for both gases, are easy to regenerate and cheap.
- Fe_3O_4-graphene and MOF-117 based NPs have reported the highest CO_2 sorption capacities.
- IRMOF-6, MOF-177 and MOF-5 showed the highest adsorption capacities for CH_4.
- Further studies are needed to prove their long term efficacy in real applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Innovative gas capture technologies with the objective to mitigate CO_2 and CH_4 emissions are discussed in this review. Emphasis is given on the use of nanoparticles (NP) as sorbents of CO_2 and CH_4, which are the two most important global warming gases. The existing NP sorption processes must overcome certain challenges before their implementation to the industrial scale. These are: i) the utilization of the concentrated gas stream generated by the capture and gas purification technologies, ii) the reduction of the effects of impurities on the operating system, iii) the scale up of the relevant materials, and iv) the retrofitting of technologies in existing facilities. Thus, an innovative design of adsorbents could possibly address those issues. Biogas purification and CH_4 storage would become a new motivation for the development of new sorbent materials, such as nanomaterials. This review discusses the current state of the art on the use of novel nanomaterials as adsorbents for CO_2 and CH_4. The review shows that materials based on porous supports that are modified with amine or metals are currently providing the most promising results. The Fe_3O_4-graphene and the MOF-117 based NPs show the greatest CO_2 sorption capacities, due to their high thermal stability and high porosity. Conclusively, one of the main challenges would be to decrease the cost of capture and to scale-up the technologies to minimize large-scale power plant CO_2 emissions.

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Contents

1. Introduction

1.1. Greenhouse gases – problem statement

Global Warming (GW) is the result of the increased concentration of Green House Gases (GHGs), primarily carbon dioxide (CO_2) and methane (CH_4), but also of nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluorocarbon (F_6C). The GHGs that are most abundantly emitted today are CO_2 (56%) and CH_4 (18%) (Houghton et al., 2001; McCarthy, 2001). As CO_2 is the most important gas in terms of amounts emitted, it has been widely studied (Pacala and Socolow, 2004).

CO_2 is produced in many industrial processes (i.e. fossil fuel power plants) including new prospective areas, such as the purification of hydrogen from biomass. Fossil fuel power plants are the largest point sources of CO_2 emissions (40% of total CO_2 emissions) (D'Alessandro et al., 2010); thus, they are the main targets for imminent CO_2 reduction (Doman et al., 2010; Metz et al., 2005).

Atmospheric concentrations of CH_4 (~1800 ppb) are currently much higher than those in preindustrial levels (~680–715 ppb) (Butler and Montzka, 2012). Anthropogenic CH_4 emissions account for 50–65% of the global CH_4 budget of ~395–427 TgC y^{-1} (526–569 Tg CH_4) (Kirschke et al., 2013). It is estimated that the principal CH_4 anthropogenic sources are (i) livestock (enteric fermentation and manure management), (ii) natural gas production and distribution, (iii) landfills, and (iv) coal mining (EPA, 2016). Also, it is reported that a rise in natural wetland emissions and fossil fuel emissions probably accounts for the renewed increase in global methane levels after 2006, although the relative contribution of these two sources remains uncertain (Kirschke et al., 2013).

The most convenient path towards lower CO_2 concentrations in the atmosphere would be to strongly reduce CO_2 emissions through cleaner and more environmentally friendly industrial processes. However, it is not expected that this can be achieved in the imminent future (Ciferno et al., 2009). Several options exist to reduce CO_2 emissions, such as demand-side conservation, supply-side efficiency improvement, increasing dependence on nuclear and renewable energy, and implementation of Carbon Capture and Storage (CCS) systems (D'Alessandro et al., 2010; Ciferno et al., 2009; Spigarelli and Kawatra, 2013; Yang et al., 2008).

The CO_2 capture is preferred to be applied directly on-site, since the capture materials and technologies have demonstrated better performances at high CO_2 concentrations rather than at atmospheric levels (400 ppm in 2014, Mauna Loa Observatory) (Baltrėnaitė et al., 2016).

1.2. Capture of GHGs via sorption

The storage of CH_4 on adsorbents has been pursued actively as an alternative to high pressure compressed gas storage. Thus, the use of adsorbent materials, such as activated carbons and zeolites for the storage of natural gas at low pressures, has also been reported (Solar et al., 2010). However, it was concluded that none of those conventional adsorbents showed sufficient CH_4 storage capacity to meet that required for commercial viability (Saha et al., 2010). Advanced materials have been investigated as potential CH_4 adsorbents including modified activated carbons, metal-organic frameworks (MOFs) and other porous polymers (Kizzie et al., 2014).

The technologies based on adsorption processes, such as activated carbon, zeolites and mesoporous silica, present limitations on the CO_2 retention capabilities per adsorbent mass (Cinke et al., 2003; Lu et al., 2008; Smart et al., 2006). In this sense, there is a widespread interest in the development of advanced adsorbent materials with better characteristics than conventional materials and with a specialized functionality for each pollutant.

Since CH_4 often co-exists with CO_2 in gaseous mixtures, such as natural gas, biogas and landfill gas, selective removal of CO_2 is an important process to upgrade the energy content of those mixtures (Li et al., 2013).

Nanotechnology can be defined as the engineering of functional systems "designed to measure" molecular scale. One of the benefits of these nanomaterials is the high surface to volume ratio and the ability to be synthesized with specific physicochemical properties. Nanotechnology has been applied in various areas of environmental sciences, such as catalysis, sensors and water treatment (Birgisson et al., 2012).

Several articles on water purification processes using NPs have been published focusing on the removal of metals (Contreras et al., 2015; Recillas et al., 2010; Sánchez et al., 2011; Xu and Zhao, 2007) or nutrients (Abo Markeb et al., 2016a; Abo Markeb et al., 2016b; Choe et al., 2000; Sá et al., 2009). This shows the potential of nanotechnology to remove contaminants. Only recently, certain nanomaterials, namely the metal-organic frameworks (MOFs), have achieved satisfactory CO_2