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Geopolymers as solid adsorbent for CO_2 capture

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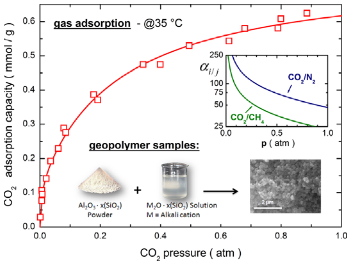
HIGHLIGHTS

- Alkali-bonded porous monoliths (geopolymers) are prepared and characterized.
- The CO_2 and light gas adsorption capacity of the geopolymer monoliths is analyzed.
- Measurements revealed a quite good CO_2 adsorption capacity.
- Measurements revealed an excellent CO_2/N_2 and CO_2/CH_4 capacity selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

Geopolymer materials, a new class of alkali-bonded ceramics, have been prepared in monolith porous form, in order to investigate the adsorptive performances of CO_2 and light gases (CH_4 and N_2) by means of a volumetric method in the sub-atmospheric pressure range. The samples have been produced by reacting an aluminosilicate powder with an aqueous alkali silicate solution, in different dilution proportions, achieving very high geopolymerization conversion (higher than 97%). The monoliths microstructural and textural properties have been first characterized by SEM and porosimetric measurements, which revealed the structure of the geopolymer as mainly consisting of nanoprecipitates and mesopores, with overall porosity from 30% up to 60%, and BET surface area up to 50 m^2/g.

The analysis of the gas adsorption properties showed a quite good capacity for CO_2 in the geopolymer monoliths, remarkably higher than those of CH_4 and N_2, pointing out the significant ability in the selective capture of CO_2 of these geopolymers. The values of selectivity in capacity obtained from the adsorption measurements, up to 200 and 100 for CO_2/N_2 and CO_2/CH_4 separation, respectively, are considerably higher than those of most of the adsorbent materials commonly accounted for in such applications.

1. Introduction

The mitigation of the greenhouse effect by fossil fuels dictates the adoption in the near future of measures for limiting the emissions of carbon dioxide in the atmosphere (Figueroa et al., 2008). So far, the post-process CO_2 uptake and its sequestration in the underground are being intensively investigated for retrofitting of industrial processes, such as, among the others, in coal-fired power plants. On the other hand, the removal of CO_2 from gaseous steams has a great relevance in the use of e.g. biogas, in which the content of methane has to be upgraded, in order to be employed as renewable alternative to conventional fuels (Bauer et al., 2013). For the capture step, four different possibilities are available (Abanades et al., 2015): i) wet chemical absorption (Olajire, 2010); ii)

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dry chemical absorption (Blamey et al., 2010); iii) physical adsorption (Samanta et al., 2012; Wang et al., 2011); and iv) separation by means of membranes (Luis et al., 2012). The impact with the industrial process, the efficiency of CO_2 uptake, the economic penalties, and the environmental impact/risk are strongly correlated with the adopted solution (Haszeldine, 2009; Finkenrath, 2012).

Among these possibilities, the physical adsorption can be effective for CO_2 uptake in the low-medium temperature range (20–200 °C), under atmospheric or higher pressure. This stage can be carried out by using a suitable adsorbent material having large superficial area and a well-developed open porosity. In most of cases, the sorbent is shaped in particles or granules for the sake of easy operation in handling and storage. Thus, the adopted material should have rather high mechanical resistance towards abrasion and be resistant to rapid changes of temperature/pressure, when pressure or temperature swing methods are adopted for the sorbent regeneration and CO_2 release. Zeolites, activated carbons, and the newly developed materials such as Metal Organic Frameworks (MOFs) are the most used adsorbents (Wang et al., 2011; Raganati et al., 2014). The figure of merit for a sorbent is the specific CO_2 adsorption capacity (mole CO_2 per kg of material), which strongly depends on the molecular structure and the material morphology, as well as on temperature/pressure of the uptake step. The easiness of sorbent regeneration, and the kinetics of the process are also of relevance.

Geopolymers are amorphous three-dimensional alumina-silicate binder materials that may be produced in the temperature range 20–120 °C by alkaline activation of alumina-silicates (Davidovits, 1991). Although the metakaolin is the most reactive raw material in alkaline environment (Panagiotopoulou et al., 2007), any alumino-silicate compound can undergo geopolymerization under tailored conditions. Apart from natural minerals and calcined clays, many industrial wastes are suitable for geopolymerization. In particular, coal ashes are good ingredients for producing geopolymers with different characteristics depending on both the ash chemical composition and temperature at which they were produced (Papa et al., 2014). Since the microstructures and properties of geopolymers depend on the nature of initial source materials, the final use of the geopolymer can be purposely designed. The presence of different scales of porosity can be relevant for improving the performance of the sorbent. In micropores, the effective gas diffusivity may assume rather low values, so the contemporary presence of a diffused mesoporosity (1 nm size) contributes to maintain the gas diffusion at level close to that of unconfined system (Dadvar and Sahimi, 2007). Conversely, the role of macroporosity would be beneficial for limiting the pressure drop in fluxed sorbent monoliths. This can be obtained by applying shaping and foaming methods (Landi et al., 2013) for producing porous granules still having good mechanical properties. In addition to the utilization in civil sector (cements, boards, bricks, etc.), the geopolymers were also tested for adsorption/purification of contaminated water (Li et al., 2006; Zhang et al., 2013), as support for catalysts (Sazama et al., 2011), and as sealant of CO_2 deposits (Nasvi et al., 2013). Recently, a one step method (Duan et al., 2015) was proposed for the synthesis of zeolite A ($Na_{12}(AlO_2)_{12}$) starting from metakaolin geopolymer gels, thanks to the affinity of the two materials. Nonetheless, the literature on the adsorption capacity and selectivity of geopolymers for gases, more specifically for CO_2, is lacking. In this concern, the intrinsic mesoporosity, the quite high superficial area (50–100 m^2/g), in combination with their relevant good mechanical properties (Young modulus of about 5 GPa and compressive strength in the range 20–90 MPa, as reported by Duxson et al., 2005; 2007a, b), make the geopolymers potential candidates for industrial processes, as solid adsorbents.

Therefore, this work reports for the first time the characterization of geopolymers as adsorbent material for the capture of CO_2. The experimental results of tests carried out at low temperature (35 °C) by means of a volumetric method are reported and discussed in the paper, along with the analysis of the ability of such material in selectively capture CO_2 with respect to lighter gases, namely N_2 and CH_4.

2. Experimental

2.1. Material preparation

The geopolymer materials are prepared using an alumino-silicate raw powder and alkali aqueous solutions $H_2O/K_2O \cdot 2SiO_2$ in different dilution proportions. The resulting alkali-bonded ceramics are classified as (K)poly(sialate-siloxo), K-PSS (Davidovits, 1991, 2008), having an atomic ratio of Si/Al=2, and potassium is the alkaline cation. Potassium silicate solutions with molar ratios SiO_2:K_2O=2.0 and H_2O:K_2O=10.0, 13.5 and 23.0 are prepared by dissolving KOH pellets (purity >85% from Sigma-Aldrich) in distilled water, and by adding fumed silica powder (99.8% from Sigma-Aldrich) under magnetic stirring. Geopolymer matrices with SiO_2:Al_2O_3 molar ratio equal to 4.00 are prepared by mechanically mixing a commercial metakaolin powder (grade M1200S, Imerys) with the $H_2O/K_2O \cdot 2SiO_2$ aqueous solutions for 20 min at 100 rpm. The resulting slurries (G10, G13 and G23) are then placed in plastic molds and cured in a heater at 80 °C for 24 h. The assessment of the CO_2 adsorption ability is carried out on the resulting monoliths as prepared or after shaping or crushing into granules of desired sizes.

The geopolymers synthesis has been detailed in a previous work (Landi et al., 2013), which demonstrated the versatility of the process in producing materials with different chemical-physical properties, morphologies and micro- and macrostructures.

The degree of geopolymerization of the produced geopolymer resulted very close to unity, around 97% (Landi et al., 2013). However, unreacted residual of potassium silicate could be present, so that repeated washing steps are carried out in deionized water and vacuum in order to ensure the complete removal of such residues. Indeed, the unreacted residuals of potassium disilicate can slowly react with the CO_2 diffusing in the geopolymer samples, eventually forming carbonate species, and leading to inconsistent results of the adsorption performances. Shortly after the washing step, the monoliths are then conveniently dried under vacuum at 120 °C for about 24 h.

2.2. Morphological characterization

The morphological and microstructural features of geopolymer specimens are examined by Scanning Electron Microscope, SEM-FEG (Zeiss), on uncoated samples.

Pore size distribution in the range 0.0058–100 μm is analyzed by mercury porosimetry, MIP (Thermo Finnigan Pascal 140 and Thermo Finnigan Pascal 240), whereas measurements of the specific surface area have been carried out in a Thermo Scientific™ Surfer instrument. The specific surface area is calculated by the Brunauer–Emmett–Teller (BET) method, by means of nitrogen adsorption at 77 K. Porosimetric and surface area analyses are carried out on massive samples (portion of monoliths). The experimental error of such measurements is mainly due to the accuracy of Hg intrusion porosimetry (4%) and that of the specific surface analyzer (1%).

2.3. Gas adsorption measurements

Gas adsorption tests are carried out in a pressure decay