

Preparation of thermally stable geopolymers as new catalysts or supports

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Introduction

Geopolymers are alkali bonded ceramics (ABC's) and are produced using an energy saving process involving chemical reactions in aqueous medium at $T < 120^\circ\text{C}$. Thermally stable geopolymers may have many industrial applications, considering that their preparation allows to produce near-net-shape pieces, also simultaneously to the foaming. ABC's have a three-dimensional aluminosilicate network, in which polymeric Si-O-Al-O bonds form under alkaline conditions in presence of aluminosilicates. The final structure of a fully reacted ABC consists of nanoparticles ranging from 5 to 15 nm, pores of 3 to 10 nm with specific surface area in the range 20-140 m^2/g . Finally, the functional and structural properties of the ABC's can be tailored by introducing specific ceramic fillers. The geopolymer network and the zeolite framework have close similarity in the exchange with charge balancing cations; ABC's network also enables incorporation of transition metal ions or protonic extra-network sites as active centres for catalytic reactions [1]. However, it must be noted that geopolymers possess some advantages in comparison to zeolites, such as formation at room or low temperature, mesoporosity and low preparation cost, opening potential interests for the synthesis of new robust catalysts for heterogeneous reactions. Aim of this study was to set up the preparation method for new geopolymers (pellets and/or foams) to be applied as catalysts or supports.

Experimental

Commercial kolins after calcination or, directly, meta-kaolins were used to prepare the geopolymeric materials, by reaction with potassium silicate solutions, with the following molar ratios: $\text{SiO}_2:\text{K}_2\text{O} = 2$ and $\text{H}_2\text{O}:\text{K}_2\text{O} = 23$. The role of the raw materials and reaction parameters were deeply investigated (XRD, thermal analyses, SEM, pore distribution, MAS-NMR, etc.) in order to evidence their effects on the properties of the obtained geopolymers. Coarse corundum powder was used as main component (80 vol %) to produce geopolymeric composite foams, prepared by adding redox foaming agents to the geopolymeric slurry under mechanical mixing. The slurries were placed in plastic moulds and allowed to mature at r.t. and/or up to 80°C . Geopolymers and composites were investigated by MAS-NMR, SEM and XRD and a thermal treatment up to 1300°C were performed to check the thermal stability.

Results/Discussion

The preliminary step allowed to select the best commercial raw material and defined the right preparation method [2]. A high degree of geopolymerization is important to complete

the ionic exchange and to impart dimensional stability at high temperature. The reactivity of the meta-kaolin raw materials is related to their alkaline hydrolysis in the first step of the geopolymerization reaction. The surface area values, the degree of kaolin dehydroxylation and the amount of Al-penta-coordinated in the final metakaolins greatly affect the geopolymerization as well as the process conditions, mainly mixing and curing temperature. Figure 1 reports SEM micrographs of the microstructure achieved by manual mixing (25% geopolymerization determined by MAS-NMR) or mechanical mixing (complete geopolymerization) of the same metakaolin.

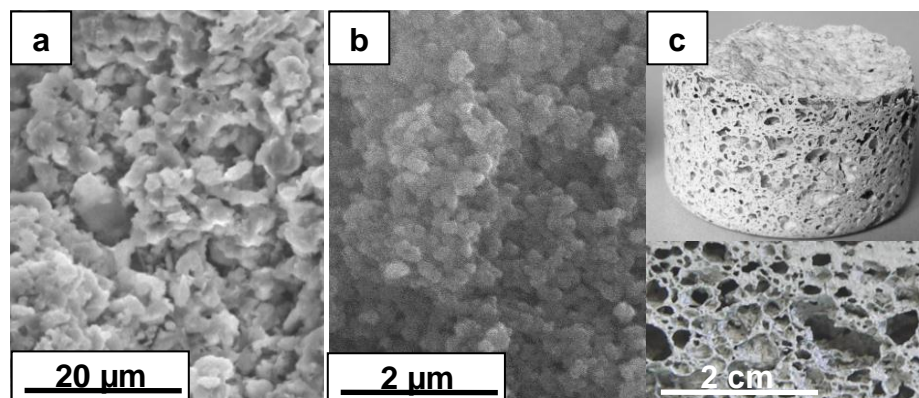


Fig. 1. (a) Partially reacted (25%), and (b) fully reacted geopolymer: (c) geopolymeric composite foam.

The high temperature linear shrinkage of geopolymeric resins and composites is low when a highly reactive metakaolin was used. Geopolymers with molar ratio $\text{SiO}_2:\text{Al}_2\text{O}_3 = 4$ have been shown to crystallize by heating in leucite, $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$, and traces of $\alpha\text{-Al}_2\text{O}_3$, as evidenced by XRD patterns. Also sanidine, KSi_3AlO_8 may be present and attributed to an incongruent melting to leucite plus liquid above 1050°C . Compositional heterogeneities, together with the presence of free alkali ions in the geopolymer structure, favour the formation of a glass-type phase. The linear shrinkage is proportional to the glass amount and the viscosity during the liquid phase sintering. The foaming conditions, the addition of foaming agents, the curing temperature and the water addition affect remarkably the dimension (from micro to ultra-macro) and amount (from few percent to 80%) of pores. An example of a geopolymeric composite foam with 80 % porosity is reported in figure 1c. After thermal treatment at 1200°C , the linear shrinkage is near to zero.

References.

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2. V. Medri *et al.*, *App. Clay Sci.* **50** (2010) 538.