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Research paper

Hydrothermal synthesis of zeolites using sanitary ware waste as a raw material

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ABSTRACT

Zeolites are extensively produced by hydrothermal treatment of different raw materials, such as kaolin. Sanitary ware (SW) is a kaolin-based ceramic ware usually found in sinks, urinals and bathtubs whose production is led by Spanish domestic clay product industry. SW production generates approximately 8% of solid waste in Spain, which increases landfills sizes and pose economic, social and technical problems.

This study aims to evaluate the feasibility of solid waste of SW industry to produce zeolites once subjected to a conventional hydrothermal treatment during different times and temperatures. Ground SW was subjected to dissolution in a highly basic medium (NaOH 5 M) inside a Teflon-lined stainless steel reactors, at temperatures of 100, 150 and 200 °C for 1 to 30 days. X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to characterize both the raw material and resultant mineral phases. Quartz and mullite present in SW transform into zeolites, as temperature and time increase. Mineral assemblage at 100 °C includes zeolite P, Na-faujasite and sodalite as major component and analcime, natrolite, and zeolite A as minor, which behave as metastable phases and their relative abundance depends on aging time. Analcime and cancrinite crystallization is favored by high temperature (150 °C to 200 °C) and increasing aging time produces analcime disappearance. Cancrinite is the dominant mineral after 30 days.

Conventional SW waste is an optimal raw material for zeolites synthesis under high alkaline hydrothermal conditions. Combining time and temperature it is possible to drive crystallization towards a target phase.

1. Introduction

Zeolites are crystalline, microporous, hydrated aluminosilicate minerals widely used in numerous technical applications mainly as catalysts, adsorbents and ion exchangers that can be classified into natural or synthetic materials and have demonstrated to be useful in industry, agriculture, veterinary, human health as well as for environmental remediation and protection.

Synthetic zeolites can be obtained using several source materials, both natural and synthetic, as well as from pure chemical reagents. In any case, the starting material(s) or chemical(s) must be a rich source of Si and Al. A wide variety of different materials have been studied for the synthesis of zeolites, most of them considered as waste materials produced by different industries. Particularly, the use of waste materials as starting sources of alumina and silica contributes to the reduction of environmental problems and minimizes zeolites production costs, which are considered high valuable minerals. Among the substrates studied in recent years it is possible to mention fly ash (Belviso et al., 2012, 2015a, 2015b; Cardoso et al., 2015a, 2015b; Aldahri et al., 2016; Ojumu et al., 2016), other zeolites (Covarrubias et al., 2006; Honda et al., 2014; Behin et al., 2016), asbestos (Saada et al., 2009), perlite (Wang et al., 2007) and less commonly diatomite (Chaisena and Rangsriwatananon, 2005; Garcia et al., 2016), red mud (Belviso et al., 2015a), rice husk (Petkowicz et al., 2008; Atta et al., 2012), oil shale ash (Fernandes-Machado and Malachini-Miotto, 2005) and aluminum foil (Bayati et al., 2008). Apart from fly ashes, clay minerals highlight as proper zeolites raw materials (Yue et al., 2014; Liu et al., 2015), more particularly kaolinite (Covarrubias et al., 2006; Mignoni et al., 2008; Ríos et al., 2009; Atta et al., 2012; Mackinnon et al., 2012; Belviso et al., 2013; Yue et al., 2014; Belviso et al., 2015b; Shams and Ahi, 2013; Wang et al., 2013, 2014; Prokof'ev and Gordina, 2014; Zhou et al., 2014; Ayele et al., 2016; Maia et al., 2015; Tang et al., 2016; Villaquirán-Caicedo et al., 2016). Johnson and Arshad (2014) recently reviewed the hydrothermal synthesis of zeolites based on kaolinite as raw material and analyzed the main factors governing the process.

Hydrothermal treatments are the bases of zeolites synthesis procedures. In order to improve the efficiency of the processes, new techniques have been recently applied, such as ultrasonic techniques (Shams

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and Ahi, 2013; Behin et al., 2016; Bukhari et al., 2015, 2016; Vaičiukynienė et al., 2015; Aldahri et al., 2016; Ojumu et al., 2016; Jusoh et al., 2017) and microwave-assisted procedures (Chandrasekhar and Pramada, 2008; Youssef et al., 2008). Two main hydrothermal treatments can be distinguished: (i) the conventional hydrothermal procedure (Petkowicz et al., 2008; Saada et al., 2009; Chandrasekhar and Pramada, 2001; Heller-Kallai and Lapides, 2007; Lapides and Heller-Kallai, 2007; Alkan et al., 2005; Bayati et al., 2008; Mackinnon et al., 2012; Jha and Singh, 2014; Cardoso et al., 2015a, 2015b; Maia et al., 2015; Prokof'ev and Gordina, 2014; Wang et al., 2010, 2013; Covarrubias et al., 2006; Wang et al., 2014; Tang et al., 2016; Garcia et al., 2016) and (ii) the alkaline fusion followed by hydrothermal reaction (Wang et al., 2016; Ríos et al., 2009; Ayele et al., 2016; Belviso et al., 2012, 2013, 2015a, 2015b; Liu et al., 2015; Molina and Poole, 2004). In both cases the reactions occur in a highly basic medium (pH > 10) but the main difference lies in the state of the alkaline substance: in the first (i) the aluminosilicate solid raw materials are mixed with an alkaline solution, while in the second (ii) the raw materials are mixed with a solid basic compound and thermally activated by fusion.

Sanitary ware is a ceramic ware usually found in sinks, urinals and bathtubs. SW production is led by Spanish domestic clay product industry (Medina et al., 2012). The traditional sanitary ware vitreous body composition is made up of 50 wt% clay minerals (mainly kaolinite), 25 wt% quartz and 25 wt% feldspar, known as the “tri-axial white ware”. After the firing process (1250 to 1290 °C) water is released and crystalline networks of the raw materials are destroyed to give rise to metastable and new crystalline components (Medina et al., 2012). During the sintering of a porcelain body, clay minerals (such as kaolinite) transform themselves into mullite, thus giving plasticity and mechanical strength to the product. On the other hand, feldspars are fluxing agents and quartz acts as a filler, maintaining the structure during sintering. This final composition makes SW apparently ideal for zeolites synthesis due to the high quantity of Si and Al. $ZrSiO_4$ is added in order to enhance the opacity of SW, especially in the presence of ZnO, although ZrO_2, ZnO, TiO_2, and SnO_2 are also used as opacifying agents. They also provide an increase in whiteness and shine, which are valuable commercial properties (Boudeghdegh et al., 2015). Industrial production of sanitary ware generates approximately 8% of solid wastes in Spain, which increase landfills sizes and pose economic, social and technical problems (Medina et al., 2012). Therefore, any usage that could be given to these materials will help minimize these problems.

Chamotte obtained by grinding solid waste derived from the sanitary ware production could be used as an appropriate raw material for hydrothermal zeolite synthesis due to its chemical and mineralogical composition. That could contribute to minimize environmental problems associated to industrial ceramic wastes. Zeolites synthesis literature, however, does not report the use of SW solid waste as a raw material. The aim of the present study is to evaluate the feasibility of SW to produce zeolites once subjected to a conventional hydrothermal treatment at several aging times (1–30 days) and temperatures (100–200 °C) and to identify and characterize the resulting mineral phases.

2. Materials and methods

Commonly used sanitary ware was obtained in large pieces, as a construction waste material. SW pieces were washed with distilled water and ethanol and then pulverized in order to obtain small and homogeneous particle sizes (smooth powder). Firstly, SW was crash into irregular and large pieces with an iron mortar and then with a jaw crusher (Retsch®, BB200). After this, SW was grinded during 20 min in a mechanic mortar grinder and finally the resulting powder was subjected to grinding in a vibratory disc mill (Retsch®, RS 200) equipped with agate rings.

SW sample was characterized by X-ray powder diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

X-ray diffraction (XRD) was carried out using a PANalytical X'Pert Pro diffractometer equipped with an X'Celerator solid-state detector and a sample holder spinning. X-ray powder diffraction patterns were recorded using random oriented mounts with CuKα radiation, operated at 45 kV and 40 mA, in the range 3–70°2θ. Semi-quantitative estimation of the solid composition in crystalline phases was obtained by X'Pert HighScore Plus (PANalytical, 2005), on basis of the Reference Intensity Ratio (RIR) values (Chung, 1974a, 1974b; Chung, 1975). TOPAS (Bruker, 2014) software was used to estimate the degree of crystallinity (DOC), also reported in literature as crystalline index. The DOC method is based on the estimation of the total intensity or area contributing to the overall diffraction pattern by each component in the analysis. We used the following formulae:

$$DOC = \frac{Cristalline\ Area}{Crystalline\ Area + Amorphous\ Area}$$

Integrated areas under the Bragg peaks and amorphous band were measured by a profile fitting procedure using TOPAS, taking into account the background. The weight fraction of the amorphous material, $W_{amorphous}$, can be calculated from:

$$W_{amorphous} = 1 - DOC$$

Chemical analysis by X-Ray fluorescence (XRF) was performed using a Bruker® S4 Pioneer equipment, with LIF200, PET, OVO55 lens, a Rh anode X-ray tube and operated at 60 kV and 150 mA. Elements (Si, Al, Ti, K, Mg, Fe, Na, Ca, Mn, P, Zr, Sr) were measured as fused beads using glass discs by fusing 0.9 g of SW in lithium tetraborate. The quality of the analysis was monitored by measuring 25 different reference materials whose standard deviation are < 0.3% for Si, < 0.05% for Na, Mg, Al and Fe and a < 0.010% for K, Ca, Ti and 10 μg/g for trace elements. Reproducibility was higher than ± 0.05% for both major and trace elements.

Fourier-transform Infrared Spectroscopy (FTIR) was performed using a PerkinElmer Spectrum One spectrometer equipped with a lithium tantalate ($LiTaO_3$) detector. Each sample was diluted in KBr to obtain 1% (w/w) pellets and were recorded in absorbance mode in the 4000–400 cm^{-1} range with a wavenumber resolution of 4.0 cm^{-1}. A total of 100 scans were collected for each spectrum at a scan speed of 0.2 cm/s.

SEM observation were performed with a Zeiss Supra 40VP microscope operated under high-vacuum conditions, equipped with an energy dispersive X-ray detector (EDS). Before examination, sample was suspended in water and filtered through a polycarbonate filter (pore diameter of 0.2 μm); a piece of the filtered sample was mounted on a stub with a graphite ribbon and then carbon-coated. Samples were investigated using secondary (SE) and backscattered electron (BSD) detectors.

Hydrothermal synthesis process was performed in 50 mL Teflon-lined stainless steel reactors (Parr 4744). The reactors were heated in an oven and the pressures inside reactors corresponded to vapor water pressure at all working temperature. Powdered SW (2 g) was hydrothermally activated in NaOH 5 M solution (10 mL), by heating at prefixed temperatures (100, 150 and 200 °C). Aging times varied from 1 day to 30 days. At the end of each experiment, the reactors were cooled quickly with water to quench the reaction, and solid and solution were immediately separated by centrifugation (15 min., 5000 rpm). Solids were repeatedly washed with pure water (MilliQ grade) by 10 cycles of centrifugation (also 5000 rpm, 15 min.) and dried in an oven at 50 °C. Finally, each sample was manually grounded and stored in plastic vials at room temperature. No specific precautions were taken to control the influence of environmental CO_2 during the hydrothermal synthesis.