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Synthesis of zeolite Y from diatomite as silica source

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ABSTRACT

Bolivian diatomite was successfully used as a silica source for the synthesis of zeolite Y. Prior to synthesis, the diatomite was leached with sulfuric acid to remove impurities and aluminum sulfate was used as an aluminum source. The raw materials were reacted hydrothermally at 100 °C in water with sodium hydroxide and different Na_2O/SiO_2 ratios were investigated. The final products were characterized by scanning electron microscopy, X-ray diffraction, gas adsorption and inductively coupled plasma-atomic emission spectroscopy. Diatomites originating from different locations and therefore containing different types and amounts of minerals and clays as impurities were investigated. After optimization of synthesis time, zeolite Y with low SiO_2/Al_2O_3 ratio (3.0–3.9) was obtained at a high yield for high alkalinity conditions ($Na_2O/SiO_2 = 0.85$–2.0). Lower Na_2O/SiO_2 ratios resulted in incomplete dissolution of diatomite and lower yield. Nevertheless, decreasing alkalinity resulted in a steady increase of the SiO_2/Al_2O_3 ratio in zeolite Y. Consequently, it was possible to synthesize almost pure zeolite Y with a SiO_2/Al_2O_3 ratio of 5.3 for a Na_2O/SiO_2 ratio of 0.6, albeit at a low yield. In this respect, diatomite enables the synthesis of high silica zeolite Y and behaves similarly to colloidal silica in traditional syntheses, with both sources of silica having in common a high degree of polymerization. Interestingly, the presence of minerals and clays in the starting diatomite had marginal effects on the outcome of the synthesis. However, their dissolution resulted in presence of calcium and magnesium in the zeolite Y crystals. Finally, overrun of all investigated compositions resulted in the formation of zeolite P nucleating and growing onto dissolving zeolite Y crystals, which was shown to be triggered when aluminum was completely depleted at high alkalinity.

1. Introduction

Zeolites are crystalline aluminosilicate molecular sieves with unique properties. These compounds are comprised of a three-dimensional network of silicon and aluminum oxide tetrahedrons (SiO_4 and AlO_4^-) linked by shared oxygen atoms and containing charge-compensating cations. The resulting structures form porous frameworks with micropores in the range of ~2–10 Å [1], which confer them molecular sieving properties. Zeolites also possess very high surface areas due to this microporosity and exhibit variable acidic properties depending on composition. Because of these special properties, they can be used in a wide range of applications such as ion exchange, adsorption, catalysis and membrane separation [2].

Two zeolites of particular interest are zeolite X and zeolite Y. These are faujasite type zeolites (FAU), defined by a SiO_2/Al_2O_3 ratio between 2 and 3 for zeolite X and greater than 3 for zeolite Y [3]. The basic structural units for this type of zeolite are sodalite cages which form supercages able to accommodate spheres up to 1.2 nm in diameter. The openings to these large cavities are 12-membered oxygen rings with a free diameter of 7.4 Å [4]. Zeolite X can be employed as an adsorbent for CO_2 capture [5], but it is mostly used in the detergent industry to compliment or substitute zeolite A due to its high capacity for the removal of Mg^{2+} ions in hard water [6]. Zeolite Y is the most widely employed zeolite catalyst due to its use in fluid catalytic cracking (FCC) for conversion of heavy petroleum molecules into gasoline-range hydrocarbons because of its high size selectivity, high concentration of active acid sites, and thermal stability [7–9].

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Traditional methods for synthesizing FAU-type zeolites typically involve chemical grade reagents as starting materials and crystallization from a gel or clear solution under hydrothermal conditions. Typical synthesis mixtures are usually composed of sodium silicates, sodium aluminate, aluminum salts or colloidal silica in a strong alkaline media. Other processes also include seeding to obtain the desired zeolite [10]. However, synthesis of zeolites from low cost raw materials has also been investigated, since chemical grade reagents are expensive. Until now, the use of materials such as kaolin [11], high silica bauxite [12], halloysite [13], interstratified illite-smectite [14], montmorillonite [15], bentonite [16], and incinerated ash [17] has been reported. Of these raw materials, kaolin has been the most extensively studied, since its composition in terms of SiO_2/Al_2O_3 ratio corresponds to that of zeolite A. Consequently, an additional source of silica is required in order to increase the SiO_2/Al_2O_3 ratio for the synthesis of FAU-type zeolites from kaolin.

Diatomite, a type of siliceous biologic sedimentary rock, is an attractive raw material with high silica content. It contains mainly amorphous silicon oxide derived from biogenic siliceous sediments (unicellular algae skeletons, frustules) and is available in bulk quantities at low cost [18]. Being amorphous and silica rich, diatomite does not require any additional heat treatment or silica source for use in the synthesis of FAU-type zeolites, both of which represent additional costs [19]. However, the occurrence of $CaCO_3$ and Fe as impurities is quite common in diatomite type materials [20] and adequate treatments must be employed for purification [21]. Moreover, potassium, which is known to promote the formation of zeolite P [22], is also common in this kind of raw material meaning that a reduction in potassium content is required.

A number of groups have reported the use of diatomite as raw material for zeolite synthesis [23–26]. However, to the best of our knowledge, there are very few reports about the synthesis of FAU-type zeolites using diatomites as the silicate source. This is probably due to the difficulty of synthesizing a highly crystalline product consisting of FAU-type zeolites without contamination from zeolite P, which is often grown as a main secondary product [27]. Li et al. reported the use of diatomite to form pure zeolite Y [28]. However, a technique based on fusion and seeding was used to obtain pure zeolite Y and prevent the formation of zeolite P. Synthesis of zeolite Y with suitable properties for use in FCC was also reported Li et al. using a combination of specially treated kaolin and diatomite with a special seeding technique but without the involvement of external Al—or Si— containing chemicals [29].

In the present work, we report on the synthesis of FAU-type zeolite with different SiO_2/Al_2O_3 ratios from diatomite with high crystallinity and yield. The effect of varying the Na_2O/SiO_2 ratio and synthesis time at constant SiO_2/Al_2O_3 and H_2O/Na_2O ratios in the $SiO_2-Al_2O_3-Na_2O-H_2O$ system is discussed, as well as the influence of the diatomite purity on the final products. No energy consuming fusion and no (costly) seeds are needed in the method presented here.

2. Experimental

2.1. Materials

Diatomite originating from the Murmuntani zone, near Llica in the Potosi region of Bolivia, was used as aluminosilicate source. Three different sampling locations were investigated. The corresponding diatomite samples are herein referred to as diatomite 1 (D1), diatomite 2 (D2) and diatomite 3 (D3). Aluminum sulfate octadecahydrate in powder form ($Al_2(SO_4)_3$ * $18H_2O$, Riedel-de Haën, p.a., >99%) was employed to adjust the SiO_2/Al_2O_3 ratio to that of typical syntheses of zeolite Y. The alkalinity of the synthesis mixture was regulated with sodium hydroxide (NaOH, Sigma Aldrich, p.a., ≥98%). Silicon (Merck, p.a., >99) was used to calibrate the peak position during XRD experiments. The unit cell dimension was determined from the data and used to estimate the SiO_2/Al_2O_3 ratio in the crystals. A commercial powder of zeolite Y (Akzo Nobel, CBV100L-T) was used as reference sample for comparison of the results obtained by nitrogen gas adsorption and X-ray diffraction.

2.2. Synthesis procedure

The raw diatomites were crushed and treated with 6M H_2SO_4 at 373 K for 24 h in an autoclave under hydrothermal conditions, rinsed with distilled water until pH 7 and dried overnight [19]. During filtration, a dark sediment formed at the bottom of the glass beaker. This layer, which was found to consist of large particles of plagioclase and quartz by SEM and XRD, was discarded and only the rest of the materials having a white aspect were utilized in the next steps of processing. Acid treated diatomite (aD1, aD2 or aD3) as well as a suitable amount of $Al_2(SO_4)_3$ to adjust the SiO_2/Al_2O_3 molar ratio were added to NaOH solutions of different concentrations whilst stirring. The molar ratios of the synthesis mixtures were: $Na_2O/SiO_2 = 0.4–2.0$; $SiO_2/Al_2O_3 = 11$; $H_2O/Na_2O = 40$. These solutions were aged with stirring at room temperature in glass beakers for 24 h. At the end of the aging period, the reaction mixture was transferred to Teflon-lined autoclaves. The autoclaves were placed in an oven kept at 373 K for different periods of time. At the end of the hydrothermal treatment, the autoclaves were quenched in cold water. The solid product was separated from the reaction mixture by suction filtering using filter paper (Munktell, grade 00H). The solid product was repeatedly filtered and dispersed in distilled water until the pH of the filtrate liquid was less than 9. The final solid product was dried in an oven at 373 K overnight and weighed in order to estimate the yield.

2.3. Characterization

To determine the chemical composition of the diatomite, acid treated diatomite and final products, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed: 0.1 g sample was digested with 0.375 g of $LiBO_2$ and dissolved in HNO_3. Loss on ignition (LOI) was determined by heating the sample to 1273 K. The mineralogical composition of the raw materials and final products were determined by X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer, equipped with a PixCel3D detector and a graphite monochromator. CuKα1 radiation with $\lambda = 1.540598$ Å at 45 kV and 40 mA was used and 2θ was varied in the range 5–50° at a scanning speed of 0.026°/s. The peaks observed in the diffractograms were compared with the powder diffraction files (PDF) database. The SiO_2/Al_2O_3 ratio of the FAU zeolites was calculated by determining the lattice parameter from the (555) reflection of faujasite and using the empirical relationship proposed by Rüscher et al. [30]. Crystallinity was determined by calculating the area under the peaks in the $2\theta = 31.0–32.5°$ region after background removal and comparing it to that obtained for a commercial zeolite Y powder. The morphology of the raw materials, intermediate products and final products were studied by extreme high resolution-scanning electron microscopy using an XHR-SEM Magellan 400 instrument supplied by the FEI Company. The samples were investigated using a low accelerating voltage and no conductive coating was used. Energy dispersive spectroscopy (EDS, X-max detector 50 mm^2, Oxford Instruments) was also performed to establish the overall composition of the final products and to gain compositional information about individual zeolite Y crystals and extraneous phases. EDS analysis was carried out at 10 kV on a SEM equipped with a