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Progressive weakening of zeolite granules due to cyclic moisture loading and unloading

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ABSTRACT

The influence of moisture content and cyclic moisture loading and unloading on the mechanical properties like the strength of three different types of zeolite granules has been studied by uniaxial compression tests. The tested granules had been processed using different contents of binder and different thermal drying/activation temperatures. A moistening–drying cycle consists of moistening the granules in a climate chamber using wet air and complete immersion in a water bath followed by thermal drying in a drying chamber at 350–400 °C. The experimentally recorded force–displacement curves and digital images of the granule and fracture surfaces recorded using scanning electron microscopy are evaluated and discussed.

With increasing number of moistening–drying cycles, a continuous decrease in the strength of granules take place due to non-regenerative damage of the structure. However, a critically constant strength level is more or less reached after ten cycles.

1. Introduction

Zeolites have increasingly become important for industrial applications and are now one of the most important technical adsorbents. Moreover, their adsorption properties are used for heating and cooling processes as well as for thermo-chemical energy storage. Due to their unique structure, chemical properties and special surface texture, zeolites are also used for separation, purification and drying processes, for catalysis and as ion exchangers [1].

Zeolites occur in nature, but may also be synthesized. A review focusing on the current reports of kaolinite-based zeolites and the important factors in their synthesis has been reported by Johnson and Arshad [2]. Among the factors discussed, are the effect of SiO_2/Al_2O_3 (Si/Al) molar ratio (of the gel mixture), metakaolinization time and temperature, aging condition, alkalinity, and crystallization time and temperature.

The general empirical formula of crystalline aluminosilicates is $Mx/n[(AlO_2) \times (SiO_2)y] \cdot zH_2O$, where M is an exchangeable cation and n indicates the cation valency [1]. Zeolites can adopt many different structural forms. In Fig. 1, the structure of zeolite A is schematically shown. It is composed of primary units (PU, SiO_4- and AlO_4 tetrahedrons), which form the corner points of secondary units (SU). In combination, the SUs form tertiary units (TU) that give the zeolite, a macroscopic three-dimensional structure [3].

Between the tertiary units, hollows (which are termed as α-cages) are located to which pores lead up. The cations, contained in the zeolite, are decisive for the diameter of the pores. In the present work, zeolites in which Na + cations are present have been investigated, whereby, the uniform pore diameter of 4 Å results [3]. Also, slight deviations have been reported (see Refs. [1,4]), where the pore diameter has a value of 0.38 nm (3.8 Å). From the pore diameter (4 Å) and the structure (zeolite A), the full name of the investigated zeolite class follows: zeolite 4A.

Hecht [5] describes the production of ceramic products as a complex chemical process that is carried out by firing in an oven. During this procedure, the different mineral components give off their adsorbed moisture and chemically bound water. A change of the crystal system (e.g. quartz and kaolinite), splitting off contents (e.g. feldspar), flue gas formation due to burning of the carbon content, dissolution of crystals in the melt and eventually general softening (on reaching the maximum temperature during the firing process) occurs. During cooling down, glassy solidification, segregation of crystalline compounds and conversion of the crystal system of some substances occur. Apart from all these chemical and

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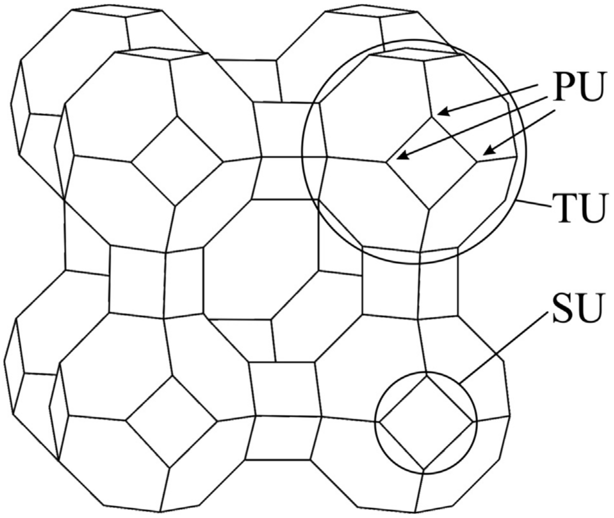

Fig. 1. Scheme of the structure of zeolite A according to Puppe and Büchner [3].

physical processes, thermal expansion develops which is significant at high firing temperatures and is also very different for each component. Besides, during heating, the described processes do not advance in the same direction resulting in terms of reduction in the mass, but some recrystallizations contributed to an increase in mass.

According to the measurements of Barrer and Meier [6], the lattice constant of the unit cell of zeolite A can increase step-wise with increasing moisture content. Moreover, Noack et al. [7] have studied the unit cell dimension for different zeolite crystals as a function of temperature and moisture content. They have found that hydrated zeolite crystals show an irregular thermal expansion and contraction which confirms the result from Tschaufeser and Parker [8]. Thereby, defects and micro cracks can develop. For example, zeolite layers of small crystals with either a random or a preferential crystal orientation relative to the support and (at regeneration) only a partial de-watering in the case of Al-rich zeolite layers can minimize the tension in the support-membrane system. Thus, the irreversible formation of macroscopic cracks can be avoided and the formation of small intercrystalline pores in the mesopore region becomes reversible.

In case zeolites are used, for example, as an adsorbent or as an energy storage system, in a mostly constant intervals, they initially adsorb water (adsorption) and subsequently release the water (desorption) under certain circumstances (high temperature, low pressure). Consequently, the granules are treated cyclically, where a cycle consists of (complete) wetting and subsequent drying. To avoid high reinvestment costs, one expects that the zeolites should exhibit a performance-wise long durability and a low variation of the material and breakage properties with change of the condition (dry/wet) [9].

The requirements for micro porous materials such as zeolites, metal-organic frameworks, activated carbons and alumina phosphates and their most important properties are described by Akthar et al. [10] regarding application in gas separation and catalysis. These materials having high inner surfaces are almost always produced as particulates. To formulate such porous powders into a desired structural shape, the authors present and discuss different processes such as extrusion and coating. Moreover, the possibilities and limitations for increasing the mechanical strength by use of inorganic binders and the most commonly used important binders (e.g. clays and silicic acid) are also described.

Zeolites exhibit a high brittleness, hence, during mechanical and thermal stressing, damage like defects and micro cracks can develop [11]. However, in spite of notable research on zeolitic agglomerates, open questions regarding the mechanical properties, in particular on the strength still remain.

The regeneration behavior (cyclic moisture loading and unloading) of zeolitic molecular sieves in natural gas dehydration units has been described by Rastelli and Shadden [12]. The mechanical strength decreases with increasing number of cycles. Upon inspection of gas dehydrators, molecular sieve beds have shown broken particles and dust. The authors assume that certain components of the binders used in standard 4A products are somewhat soluble in water.

Marigo et al. [13] have investigated the mechanical properties of ZSM5, a granular spray-dried zeolite widely used in the catalyst industry. Single particle compression was used to characterize single particle mechanical properties such as reduced elastic modulus and strength using Hertzian theory of contact mechanics. In order to evaluate the relationship between single particle mechanical properties and bulk compression behavior, uniaxial confined compression was carried out. It was determined that the Adams model [14] was suitable for describing the bulk compression.

Mueller et al. already studied in Ref. [15], the influences of moisture content (at unique wetting) and granule sizes on the strength of zeolite 4A granules. A significant relationship between moisture content and strength has been observed. By Russell et al. [16], zeolite 4A granules have also been analyzed using compression tests. The study describes the influences of granule size, moisture content and loading intensity on the energy absorption and recovery at stressing. It was shown that the force–displacement behavior fits well with the Hertz law [17] during elastic loading, the model of Tomas [18] during elastic–plastic loading and the extended Hertz law according to Stronge [19] and Antonyuk [20] during elastic unloading. Another study from Mueller et al. [21] clarifies the influence of the binder and the moisture content on the strength of zeolite 4A granules.

On the basis of these results, the present study enlightens the material and fracture properties of three different types of zeolite 4A granules with increasing moisture contents and number of moisture loading–unloading cycles. In addition, a comparison of the results of all three granule types intends to clarify the influences of binder content and the production process on the mechanical properties of the granules.

2. Product samples

The three tested granule samples of zeolite 4A have been industrially produced with zeolite powder ($Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot nH_2O$) as primary particles and clay mineral attapulgite ($(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$) as binder. They vary in the contained binder content and the production process.

The first zeolite type receives the characteristic denotation 4AA and is therefore named after the zeolite class 4A. It represents the basis of the following two modifications.

The production process of the zeolite 4AA granules is carried out in four process steps. At first, the zeolite powder and the mineral binder attapulgite are mixed. In the second step, by wet granulation, spherical granules are produced by addition of water and potentially further necessary additives. Therefore, this process step can be referred to as pelletizing. Following, the required particle size is screened out. In the final process step, the sieved zeolite granules are dried and activated for adsorption at more than 500 °C.

For the second zeolite granule type – zeolite 4AB, the same production process is used. However, the granules contain a higher