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The use of microwave irradiation for zeolite regeneration in a continuous ethanol dewatering process

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ABSTRACT

The processes of zeolite-assisted ethanol dewatering with further microwave (MW) zeolite dehydration has been studied. Both gas-phase and liquid-phase alcohol dewatering methods yielded absolute ethanol. Kinetic study showed that these processes can be performed under dynamic conditions, which is relevant from a scale-up viewpoint. The concept of "*in situ* MW-assisted zeolite regeneration" was elaborated. Reduction of energy consumption by 1.7 times with 10-fold process time shortening has been shown for lab-scale MW zeolite dehydration, as compared to the corresponding thermal method. Hypothesis explaining the reasons of such a dramatic energy and time saving was proposed based on the diffusion theory. The influence of MW irradiation on the zeolite structure was studied by powder X-ray diffractometry. The results showed that even after 20 regeneration cycles the zeolite remained the same as the initial sample. The outlook for process scale-up has been discussed. A pilot-plant scale model for continuous ethanol dewatering by NaA zeolite with the following zeolite regeneration has been proposed.

1. Introduction

In the recent years zeolite molecular sieves have been widely used for dehydration or dewatering purposes due to their unique properties to selectively adsorb water from water containing solutions, which is especially topical in a view of growing interest to bioethanol production [1–5]. For ethanol dewatering purposes NaA or KA zeolites are most appropriate, being synthetic zeolites, since they have small aperture diameters (4 and 3 Å respectively), therefore organic molecules having two or more C atoms cannot penetrate inside the zeolite pores and remain in a liquid phase, while smaller molecules like water ones are effectively absorbed and retained by zeolites. In spite of a constantly growing interest to zeolites, most of the papers are dedicated to the study of adsorption properties of zeolites; meanwhile, there is much less information in the literature concerning zeolite regeneration. This gap, undoubtedly, should be supplied, since zeolite regeneration step is crucial from commercial viewpoint, and only efficient dehydration of water-saturated zeolites can ensure their durability and successful application at industrial scale.

The conventional technique for zeolite dehydration is high-temperature calcination [6,7], which is time and energy consuming because of low thermal conductivity of the zeolite materials. On the other hand, the temperature limitation exists, as high temperatures may cause partial or complete damage to zeolite matrix resulting in decrease in adsorption capacity and in zeolite life-time shortening [8].

For efficient zeolite dehydration and reduction of energy consumption, as well as for minimization of the stress on the zeolite structure, process parameters should be carefully selected. Gabrus et al. proposed in-situ thermal regeneration of 3A and 4A zeolites in the fixed bed after liquid-phase dewatering of aliphatic alcohols [8]. Thermal stability of zeolites, water adsorption capacity, adsorption selectivity and thermal desorption efficiency were carefully studied. The optimal conditions of zeolite dehydration were determined which allowed efficient dehydration of the studied zeolites with maintaining their adsorption capacity approximately at the same level over 30 hydration-dehydration cycles.

The proposed technique allows continuous alcohol dewatering with zeolites. Long life-time of zeolites is ensured by properly selected regeneration temperature mode. However, it seems reasonable to improve this "*in-situ*" approach in terms of process acceleration and energy costs reduction by replacing traditional

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heating sources for a novel and more efficient heating method, such as microwave (MW) irradiation, which shows excellent results when applied to chemical or physical processes [9–13]. It is known that ethanol has a good absorbing capacity towards MW irradiation [14] while water has middle one, nevertheless, MW irradiation is widely used for processing materials or reaction mixtures where water is a medium or one of the components [15,16]. Therefore, MW irradiation has proved to be a promising technique for various adsorbents regeneration [17–19] and intensification of separation processes like pervaporation or membrane distillation [20,21].

In view of the above said, there are all the grounds to predict efficient application of MW irradiation to NaA zeolite regeneration resulting in energy cuts and process intensification.

In this study the process of liquid phase ethanol dehydration and further zeolite regeneration with the use of MW irradiation were studied with a fixed bed of NaA zeolite. The aim of this study is the development of a continuous process of dewatered ethanol preparation comprising ethanol dewatering and MW-assisted zeolite dehydration; and determination of optimal process parameters ensuring minimization of energy consumption and process duration as compared to corresponding thermal processes. The effect of MW irradiation on zeolite adsorption capacity after multiple uses was also examined. Process scale-up is considered in this study as well.

2. Materials and methods

2.1. Materials

NaA zeolite was purchased from Salavat catalyst plant Ltd. (Russian Federation).

Ethanol–water solution with ethanol concentration 95 wt.% and NaA zeolite in the form of extruded cylinders 5–7 mm in length and 1.6 ± 0.2 mm in diameter were used in ethanol dewatering and zeolite regeneration experiments.

2.2. Analytical control

2.2.1. Water content determination

Water content in ethanol before and after dehydration step was determined by Karl Fisher method [22].

2.2.2. Zeolite dehydration degree determination

Concentration of the water adsorbed by zeolite and zeolite dehydration degree were determined by the gravimetric method. The saturated zeolite was subjected to calcination at 250 °C, and the amount of adsorbed water was calculated by the weight difference before and after calcination. The weight loss was calculated from the Eq. (1):

$$W = \frac{m_1 - m_2}{m_2} \times 100\%, \quad (1)$$

where m_1 is the weight of saturated zeolite (kg); m_2 is the weight of calcinated zeolite (kg).

2.2.3. Powder X-ray diffraction

Powder X-ray diffraction patterns of the initial zeolite sample and MW irradiated one were recorded with the powder X-ray diffractometer ≪Siemens D500≫ using Cu irradiation ($\lambda = 1.54184$ Å, graphitic monochromator), angular range 3–70° 2θ, step 0.02°.

2.2.4. Dielectric properties measurements

Dielectric properties of the saturated and dehydrated zeolite were measured with the use of the apparatus and methodology developed by us [23] according to the following procedure. The quarts cell ($r = 0.845$ cm, $l = 10{,}4$ cm) was placed into a cylindrical MW cavity ($r = 4.7$ cm, $l = 10.4$ cm) along the cavity axisppopopl. The resonance frequencies and cavity Q factor were measured with and without the tested samples. On the basis of the measurements results the dielectric constant ε', loss tangent tg δ and skin-layer depth were calculated.

2.3. Experimental set-up and procedure

2.3.1. MW set-up

MW zeolite dehydration was performed in a multimode MW laboratory system (MARS, CEM Corp., USA) equipped with IR sensor for temperature measurements. A typical distillation set-up was used for zeolite dehydration experiments (Fig. 1), consisting of a 250-mL round-bottom flask containing saturated zeolite and placed inside the microwave cavity, an upward glass tube (l = 30 cm, $Ø = 2.5$ cm), passing through the aperture in the upper wall of the MW cavity. A standard distillation kit for collecting water condensate, attached to the column, was placed outside the cavity. The process was conducted under slight evacuation provided by membrane vacuum pump for better removal of water vapor.

In the experiments on gas-phase ethanol dewatering, the typical distillation set-up was used, similar to that applied for zeolite dehydration (Fig. 1), with some modifications; *viz.* the zeolite-loaded column was used instead of a hollow tube, and a fiber-optic (FO) probe was applied for temperature measurements (Fig. 2). In this case ethanol–water mixture and zeolite-loaded column were exposed to MW field, while the distillation kit was placed outside of MW cavity.

2.3.2. Ethanol dewatering and NaA zeolite dehydration

Ethanol dewatering was performed by applying both gas-phase and liquid-phase approaches. According to the first method the ethanol–water mixture was distilled, with the vapors passing through a column filled with previously dehydrated NaA zeolite (Fig. 2). The following procedure was applied. Ethanol–water mixture was heated by MW irradiation to the boiling point, and the vapors passed through the column with the fixed bed of NaA zeolite. The necessary ratio of zeolite to ethanol–water mixture was calculated on the basis of NaA adsorption capacity determined previously (see Section 3.1), with the 20% surplus of zeolite. Due to high selectivity of NaA zeolite to water, larger molecules of ethanol were not retained and freely passed through the column, condensed and finally were collected in the receiver.

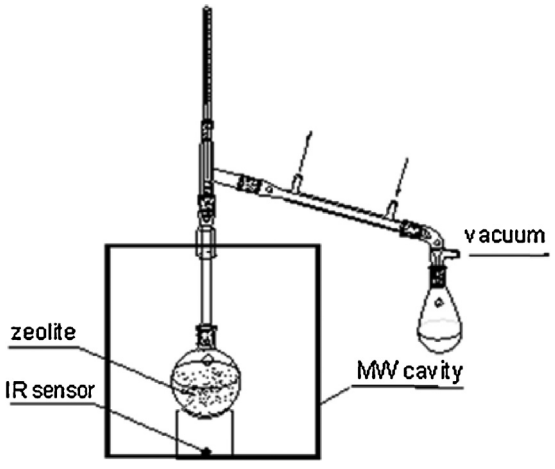

Fig. 1. Schematic image of experimental setup used for MW zeolite dehydration.