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Determination of faujasite-type zeolite thermal conductivity from measurements on porous composites by laser flash method

Lisha Wang [a,b,*], Michael Gandorfer [b], Thangaraj Selvam [a], Wilhelm Schwieger [a]

[a] Friedrich-Alexander-University Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany
[b] Joint Institute of Advanced Materials and Processes, Dr.-Mack-Str. 81, 90762 Fürth, Germany

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ABSTRACT

An approach of determining thermal conductivity of zeolite is introduced, due to the lack of its thermal properties data for heat transfer calculations in adsorption and catalytic applications. Faujasite (FAU) as one of the important zeolites, whose framework consists of sodalite cages with pores formed by 12-membered rings, was chosen as model zeolite. Pellet-shaped samples made of FAU-type zeolite and binder pseudoboehmite were prepared with different binder fractions and porosities. Apparent thermal conductivity was determined using laser flash method. Results showed that the use of pseudoboehmite increased material's heat capacity, thermal diffusivity and conductivity, and the apparent thermal conductivity of porous composites decreased with porosity. The thermal conductivity of FAU-type zeolite at 20 °C and 1 atm. was found to be 0.10 W/(m·K) by extrapolating measurement results.

1. Introduction

Zeolite-based materials are important adsorbents and catalysts in various industrial processes [1]. Their thermal properties are of great – however sometimes underestimated – importance, when the heat transfer behavior of a process needs to be evaluated and optimized, especially in heat transformer units like adsorption heat pumps. However, there is a lack of knowledge of zeolite thermal conductivity. Just few publications have provided apparent thermal conductivity (λ_{app}) values, which are dependent to measurement method and material properties like particle size, density, porosity, etc. The most often used measurement methods include hot-wire [2–4], 3ω [5], and laser flash [6]. Also, theoretical values based on simulations are much higher by ignoring the effects of realistic conditions like boundary resistance and filling gas [7]. Therefore, for zeolites, there is no reliable solid thermal conductivity (λ_{solid}) values as intrinsic properties, which becomes one of the main problems in heat transfer calculations [8].

Experimental investigations in this letter used binder fraction and porosity as independent systematic variables to examine the apparent thermal conductivity of zeolite-containing composites. Based on generalizing and extrapolating these experimental series to the boundary conditions, e.g. zero pore volume and pure zeolite composition, the solid thermal conductivity of zeolite itself was calculated. Such intrinsic value cannot be achieved just by single experiment like it is usually reported in literatures. For this study, FAU-type zeolite was chosen because it's widely-applied in industry, in particular for heat transfer units. Pseudoboehmite is a common binder material for shaping zeolite into various shapes. For the first time, we present an approach of determining the thermal conductivity of FAU-type zeolite from measurements on porous composites consisting of both zeolite and binder using laser flash method.

2. Material and methods

2.1. Sample preparation

In order to manufacture zeolite-containing porous composites, slurry mixtures having zeolite FAU (NaY, Zeolyst), binder pseudoboehmite (Sasol) and peptizing agent acetic acid (VWR) were prepared [9]. As shown in Table 1, powders of zeolite and pseudoboehmite were mixed with varying weight proportions. And then different amounts of acetic acid were added to solid mixtures, because increasing amounts of pseudoboehmite required increasing amounts of acetic acid to colloid zeolite crystals with pseudoboehmite particles via surface hydroxyl groups and thus form slurry phase. Additionally, acetic acid was also used as porogen to vary the pore volume of materials [10], and different amounts were added for mixtures of the same binder fraction. Formed slurry mixtures were homogenized by stirring for one hour and then

* Corresponding author at: Friedrich-Alexander-University Erlangen-Nürnberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany.
E-mail address: lisha.wang@fau.de (L. Wang).

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Table 1
Materials used in slurry mixtures for the preparation of samples with 20–70 wt% of binder fraction.

Sample with binder fraction [wt.%]	Zeolite FAU [g/100 g solid sample]	Pseudoboehmite [g/100 g solid sample]	Acetic acid [ml/100 g solid sample]
20	80	20	150, 300, 500
30	70	30	200, 350, 550
40	60	40	250, 400, 600
50	50	50	300, 450, 650
60	40	60	350, 500, 700
70	30	70	400, 550, 750

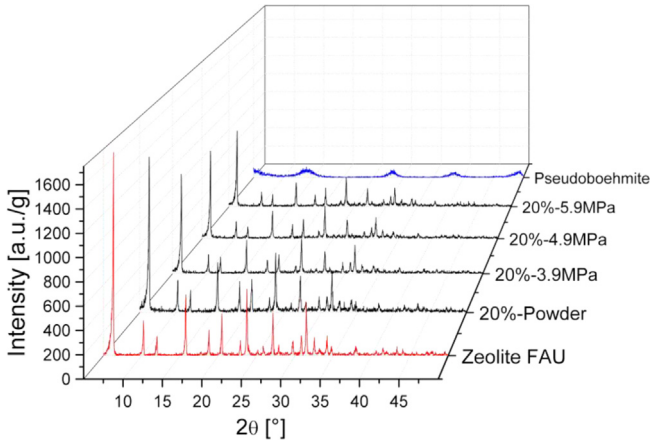

Fig. 1. X-ray diffraction patterns of zeolite FAU, binder pseudoboehmite, and mixtures with 20% binder fraction in the forms of powder and pellets (with pelletizing pressures of 3.9, 4.9 and 5.9 MPa).

dried at room temperature. Dried mixtures were transferred to mortars and gently grinded into powder samples.

For powder sample of a certain composition, one part was calcined under 500 °C for 3 h, in order to remove acetic acid. The calcined powder was then used for characterization purposes. Another part was firstly shaped into pellets of 0.1 g and 10 mm diameter with varying pelletizing pressures from 2.9 to 5.9 MPa to prepare pellets of different bulk densities [11], and then calcined under similar conditions. The loss of acetic acid generally led to the formation of macroporosity in pellets.

2.2. Characterization

Calcined powder samples were used for the following characterizations: X-ray diffraction (XRD) pattern was recorded on a Philips X-ray diffractometer using Cu-Kα radiation; solid density was measured by helium pycnometer (Pycnometic ATC, Porotec); heat capacity was determined by differential scanning calorimetry (DSC) (DSC 2010, TA Instruments) [12].

Pellet sample's porosity (P) is defined as the pore volume fraction to the bulk volume, and can be calculated by its bulk (ρ_{bulk}) and solid (ρ_{solid}) density as:

$$P = 1 - \rho_{bulk}/\rho_{solid} \cdot 100\% \quad (1)$$

2.3. Laser flash measurement

The apparent thermal conductivity of pellet sample was examined using laser flash method [13], which is applied here for composite by assuming that it behaves as homogeneous material [14]. Thermal conductivity (λ) is calculated by:

$$\lambda(T) = \alpha(T) \cdot \rho(T) \cdot c_p(T), \quad (2)$$

where thermal diffusivity (α) was measured by laser flash analysis (LFA), bulk density (ρ) was defined by its mass and bulk volume, and heat capacity (c_p) was determined by DSC.

Commercial setup Linseis LFA-1000 was used for thermal diffusivity measurement. Samples were spray-coated with graphite on both sides, in order to enhance light absorption and infrared thermal response. Evaluation software used the combined model based on Dusza [15], which considers the analytical fitting over entire temperature rise and both heat losses and finite-pulse duration effects, to calculate the apparent thermal diffusivity. Experiments were carried out at 20 °C and 1 atm. Each sample was repeatedly measured five times (deviation < 2%), and average value was taken as result.

3. Results and discussion

Fig. 1 shows the XRD patterns of zeolite FAU, pseudoboehmite, a powder sample with 20% binder fraction and three pellets made with the same composition and different pelletizing pressures. Characteristic peaks corresponding to zeolite FAU but with reduced intensities were observed for the pellets in comparison to the powder sample. This indicated that applying pressure during pelletizing could lead to slight loss of zeolite crystallinity. Nevertheless, zeolite structure remained mechanically stable under the present preparation conditions of pellets.

Heat capacity (c_p) and solid density (ρ_{solid}) are material properties, and their measurement results from powder samples could be used for pellets of the same composition. As shown in Fig. 2, both properties at 20 °C increased with binder fraction in linear fashion.

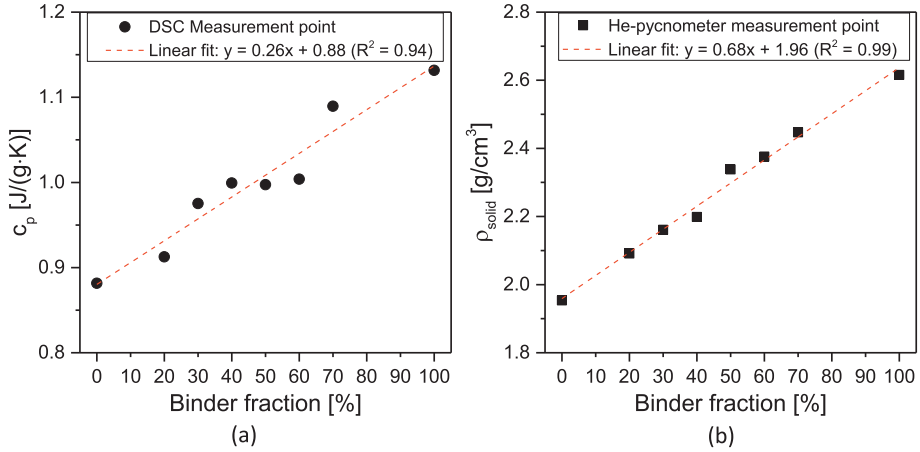

Fig. 2. Measurement results and linear fittings of (a) heat capacity and (b) solid density of powder samples (zeolite FAU with binder pseudoboehmite) at 20 °C.