Catalytic and physicochemical properties of modified natural clinoptilolite

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A B S T R A C T

A natural specimen from the deposit at Kučin (Slovakia), rich in clinoptilolite type zeolite, was dealuminated using HCl solutions of increasing concentration (0.05–11.5 M). The samples were characterized by XRD, sorption of nitrogen, TPD of ammonia, FT IR and NMR spectroscopies. The preparations modified under mild conditions (acid concentration, temperature of dealumination) retained largely their crystallinity and acidity, and were active in the liquid phase isomerization of α-pinene. Upon more severe treatments, the samples became partially amorphous and lost their catalytic activity. The kinetics of α-pinene isomerization was studied over the most active catalysts. The reaction rate constants and apparent energies of activation were obtained. Initial reaction rates over the clinoptilolite type catalysts were compared with other acidic catalysts, including ferrierite-type zeolites.

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1. Introduction

Clinoptilolite, a mineral discovered already in 1890 in USA, is the most common zeolite occurring in nature. With morphology very similar to heulandite, both zeolites reveal the same tetrahedral, aluminosilicate framework denoted as HEU, while differ in the Si/Al ratio and the alkali-dominant composition. The clinoptilolite-type framework contains three systems of mutually intersecting channels. Secondary building units forming 2-dimensional channel system in clinoptilolite/heulandite are 4–4–1. There are two channels running parallel to the *c*-axis: (i) 10-membered rings (10-MR), type A channels with the dimension of $3.0\,\text{Å} \times 7.6\,\text{Å}$; and (ii) the smaller, 8 MR channels ($3.3\,\text{Å} \times 4.6\,\text{Å}$). The third type C channels are also 8 MR and run parallel to the *a*-axis, with dimension ($2.6\,\text{Å} \times 4.7\,\text{Å}$) comparable to the B type. Crystals of clinoptilolite are monoclinic, with the space group C2/m, however sometimes the reported symmetry is lower [1,2].

It was suggested to retain two mineral names, clinoptilolite and heulandite, despite that the two zeolites are characterized by the same framework type HEU [3]. The distinction between them is made taking into account the Si/Al ratio. The more siliceous structures with the Si/Al ratios ≥4.0 are attributed to the name *clinoptilolite*, while the more aluminous isomorphs are denoted *heulandite*. Additionally, depending on the cations content, the three variety of clinoptilolite were discerned, that is

clinoptilolite-Na, -K and -Ca [1]. It was also postulated that each clinoptilolite or heulandite may be structurally different, even when exhibiting the same Si/Al ratio, the latter parameter known to affect significantly diffusion and ion-exchange of cations, sorption of gases and finally catalytic properties. The natural samples with the same Si/Al ratios might differ in silicon–aluminum ordering [4].

One of the most popular and effective methods of zeolite modification is dealumination. Dealumination of zeolites can be accomplished using either ion exchange with ammonium ions combined with (hydro)thermal treatment, or by extracting aluminum with a number of chemical agents, like organic/inorganic acids salts and other agents [5]. In this contribution we have focused on the use of a mineral acid. It should be emphasized, however, that during the acid treatment different reactions may proceed in zeolite crystals, depending on the particular conditions used (temperature, concentration of acid and contact time). At low temperatures, acid concentrations and/or short contact times replacement of the native cations by H^+/H_3O^+ ions takes place. At more severe conditions aluminum from the zeolite framework is depleted, without visible changes occurring in the zeolite structure. Finally, at still higher temperatures and acid concentrations coupled with the longer contact time advanced dealumination might be observed, leading to a partial decomposition of the zeolite crystals and formation of an amorphous phase [5,6]. First account on clinoptilolite dealumination was published by Barrer and Makki [7]. The clinoptilolite specimen from Mount Hector in California of 85–95% purity was dealuminated using hydrochloric acid; its thermal stability was exceptional, up to 750 °C. The dealuminated preparations showed increased sorption properties for water and low alcohols. However,

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sorption of benzene was the most spectacular, as it increased five times in comparison with the parent sample [7].

Isomerization of α-pinene in the liquid phase, a hydrocarbon of the monoterpene class, was chosen as a test reaction. There were several reasons for this choice. First of all, terpene feedstocks as renewable resources are becoming increasingly important for producing a variety of fine and bulk chemicals. Of these, isomers of pinene are used to manufacture a number of products for the pharmaceutical and chemical industries [8]. In particular, the isomerization of α-pinene, a reaction catalyzed by acid centers, gives bicyclic products, exemplified by camphene, and monocyclic products such as limonene and *p*-cymene (Scheme 1) [9,10]. Camphene is used for producing polymers, lacquers, explosives and medicines. Camphene is also an intermediate compound for manufacturing isoborneol, isobornyl acetate and camphor. Limonene is used in cosmetic and food products, and also as a special solvent in cars' industry. Nowadays, camphene and limonene are produced in the transformations of α-pinene, β-pinene or pinene-containing materials (e.g., wood turpentine, gum turpentine or sulphate turpentine obtained by delignification of wood) over acidic catalysts [11]. Currently, isomerization of α-pinene is carried out on an industrial scale over a weakly acidic, hydrated TiO_2 catalyst [12,13], leading to main components limonene, camphene and tricyclene, and accompanied by small amounts of fenchenes and bornylene. To prepare an active catalyst, TiO_2 is treated with sulphuric acid. In this way a layer of titanic acid supported on the oxide surface is formed. The initial reaction rate increases with the amount of H_2SO_4 used, up to a certain value, but then decreases leading to amorphous, inactive material. Consumption of a catalyst prepared in this way is about 0.6 kg per 1 t of α-pinene, however activity and selectivity of α-pinene transformations over the titania catalysts are not very high. As the reaction rate is rather low, it is important to search for a new catalytic system in order to attain better activity coupled with enhanced selectivity to desirable products [13].

A large choice of acidic catalysts, such as oxides treated with acids [14,15], modified zeolites [10,13,16–20], activated clays [21] and heteropoly acids [22,23] have been suggested in the literature for the isomerization of α-pinene. On the other hand, basic catalysts (e.g., alkaline earth-metal oxides) have been reported for the isomerization of α- to β-pinene [24].

Transformations of pinene proceed along the two parallel routes. One yields monocyclic products: limonene, terpinenes, terpinolene and *p*-cymene, while the other leads to bicyclic and tricyclic hydrocarbons, of which camphene is the most abundant and important. The reaction commences by protonation of the α-pinene double bond and forming the pinanyl cation. Then Wagner–Meerwein type rearrangement takes place leading to isobornyl and *p*-menthenyl cations. Transformation of isobornyl cations yields camphene and other bi- and tricyclic products [18,20].

Despite commercial importance, isomerization of α-pinene is a useful test reaction, as it proceeds in the liquid phase under mild conditions (60–155 °C, atmospheric pressure). α-Pinene is a relatively small molecule, comparable with benzene, with the kinetic diameter of 6.8 Å × 6.9 Å. In general, therefore, it cannot access the internal channel system of small pore zeolites, exemplified here by clinoptilolite. Whenever the mesopores are formed upon modification of clinoptilolite, then the additional pores would accommodate the α-pinene molecules thus allowing their further transformations. Taking this into account, transformations of α-pinene is a choice reaction for monitoring how a secondary pore system in zeolite is developing upon different treatments.

The objective of this work was to use a natural clinoptilolite specimen of Slovakia origin and to modify it in such a way as to obtain viable catalysts for the liquid-phase transformations of α-pinene. We have applied various treatments of natural specimen, as chemical dealumination with hydrochloric acid of different concentrations, or carrying out a multi-fold ammonium ion-exchange combined with calcination at high temperatures. The kinetics of α-pinene transformation towards camphene and limonene was studied, and the results were compared to the performance of other zeolite and non-zeolite catalysts.

2. Experimental

2.1. Preparation of the samples

Clinoptilolite sample used in this work was mined from the deposit at Kučin, Slovakia. Zeolite content in this deposit is about 83%, and the other phases present in the pristine material were low-cristobalite, feldspar and mica. The parent sample was crushed in a ball mill and sieved to obtain size fraction <250 μm, washed with distilled water (twice) and dried at 80 °C. A purified sample was dealuminated with hydrochloric acid solutions of different concentrations (0.05 ÷ 11.5 M) for 4 h at 95–97 °C. The solid:liquid ratio was always kept at 1 g of zeolite per 15 cm³ of HCl solution. The resultant samples were washed with distilled water until no Cl⁻ ions could be detected in the solution and dried at 80 °C. Before NMR measurements, the samples were hydrated in a desiccator over saturated magnesium nitrate solution. A natural, unmodified zeolite specimen was labeled HEU. The names of the other samples obtained were coined from the acid concentration used (e.g., clinoptilolite dealuminated with 0.05 M HCl was denoted as HEU-0.05HCl).

A hydrogen form of pristine clinoptilolite was prepared for comparison purposes. First, clinoptilolite purified with distilled water was transformed into the ammonium form by triple ion exchange with 10% solution of NH_4NO_3 for 4 h at 80 °C. Next, the NH_4-HEU sample was transformed into the hydrogen forms by calcination in air flow (50 cm³/min) at 300 °C (6 h), 400 °C (4 h) and 500 °C (4 h). The resultant samples were labeled H-HEU-300, H-HEU-400, and H-HEU-500, respectively. During high-temperature calcination some dealumination of the samples took place (Table 1) and new siloxane bonds (—Si—O—Si—) are formed, thereby stabilizing the zeolite framework after aluminum removal [25,26].

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the hydrated samples in the range of 5–70° 2θ were recorded on a X'Pert PRO MPD diffractometer (Panalitycal) with Cu Kα radiation (λ = 1.5406 Å). Silicon powder was used as the internal standard (ca. 5 wt.%) for calibrating the diffraction angle and estimating the crystallinity of the pristine and modified samples. Crystallinity of the samples was calculated as follows: degree of crystallinity (%) = sum total of sample's intensities/sum total of parent's zeolite intensities ×100%. Only well-separated signals were taken for estimating crystallinity of the samples. The ($h k l$) reflexes affected mostly during the dealumination were: ($0 2 0$), ($2 0 0$), ($-2 0 1$), ($-3 1 1$), ($1 1 1$), ($4 0 0$), ($-4 2 2$) and ($4 4 0$). Rietveld refinement was used for estimation the content of different phases in the pristine material. The amount of zeolite in the natural specimen was also estimated by quantitative ^{27}Al MAS NMR spectroscopy (Supplementary Data). The aluminum signal revealed the presence of two components, the largest one was due to clinoptilolite phase, and the second smaller at −59.6 ppm was assigned to feldspar. Finally, taking into account the chemical composition of the sample, Rietveld refinement and the NMR data, the following phase content in the pristine sample was obtained: 83% of clinoptilolite, 9% SiO_2 (low-cristobalite), 6% of feldspar and 2% of mica.