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Desilication of ferrierite zeolite for porosity generation and improved effectiveness in polyethylene pyrolysis

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ABSTRACT

Desilication of the medium-pore ferrierite zeolite in sodium hydroxide solutions was conducted to modify the porous structure and to create structural defects, resulting in enhanced accessibility and ultimately improved catalytic performance. Commercial H-ferrierite (Si/Al = 29) with the characteristic plate-like morphology was used as starting material. The attack by NaOH induces deaggregation, exfoliation, fracture, and ultimately perforation of the ferrierite crystals, resulting in mesoporosity of combined inter- and intracrystalline nature. The parent and treated samples were characterized by ICP-OES, XRD, N_2 adsorption, SEM, TEM, ^{27}Al and ^{29}Si MAS-NMR, FTIR, and NH_3-TPD. Optimization of the treatment conditions (NaOH concentration, temperature, and time) is required to introduce substantial mesoporosity without significantly altering the micropore structure due to excessive Si leaching. Compared to other frameworks (e.g. MFI, MTW, MOR, and BEA), FER requires harsher conditions to extract silicon leading to mesoporosity. Under optimal conditions, the mesopore surface area of the NaOH-treated ferrierite increased by a factor of 3–4 with respect to the parent zeolite, while mostly preserving the native crystallinity and acidity. The ability of NaOH to induce porosity changes in FER largely exceeds conventional dealumination post-treatments. The benefit of the introduced porosity was demonstrated in the catalytic pyrolysis of low-density polyethylene.

1. Introduction

The unique properties of zeolites, viz. crystallinity, high-surface area, acidity, ion-exchange capacity, and shape-selective character, make them hegemonic materials in many industrial applications related to catalysis, adsorption, and separation. The sole presence of micropores (0.25–1 nm) in zeolite frameworks often imposes diffusion limitations due to hindered access and slow intracrystalline transport of reactants and products to and from the bulk of the crystal [1–4]. Diffusion limitations result in a poor utilization of the zeolite volume in catalyzed reactions, limiting the activity and occasionally also the selectivity and lifetime.

Ferrierite (FER topology) is a medium-pore zeolite that is produced commercially, and it displays remarkable catalytic performance, as such or modified, in a variety of acid and redox reactions: skeletal isomerization of n-alkenes to iso-alkenes [5–8], n-paraffin cracking [9,10], dewaxing of lube oil base stocks and middle distillates by selectively hydrocracking long-chain paraffins [11], alkane hydroisomerization [12], isomerization of m-xylene [13], α-pinene [14], and dichlorobenzenes [15], isobutene trimerization [16], methanol to olefins [17], styrene epoxidation [18], propane oxidative dehydrogenation [19], NO_x reduction [20,21], and N_2O decomposition [22]. The ferrierite structure comprises an orthorhombic framework containing the main 10-MR channels (0.42 × 0.54 nm) in the [001] direction interconnected with side 8-MR channels (0.35 × 0.48 nm) in the [010] direction (Fig. 1). The intersection of the 8-MR channels and the 6-MR channels in the c-direction leads to spherical cavities (FER cage) [23,24].

Ferrierite is amenable to industrial application owing to its excellent stability toward (hydro)thermal and chemical treatments [25]. However, the reduced dimension of the pore system in relation to the size of typical substrates can be a restrictive factor to fully exploit its potential in some of the above reactions as well as to expand its application to new processes. For example, van Well et al. [26] reported that ferrierite operates as a one-dimensional pore system for long-chain molecules (C5+) and that pore blockage by coke formation results in a large inhibiting effect. In situ infrared studies by Meunier et al. [6] concluded that the n-butene isomerization was effectively limited to the acid sites located near the surface of the H-ferrierite crystals (pore mouth catalysis), while the bulk of the crystals are filled with slowly diffusing species such as branched C8 hydrocarbons and aromatics.

Diffusion limitations in zeolites can be alleviated by enlarging the micropore size or by shortening the diffusion length [4].

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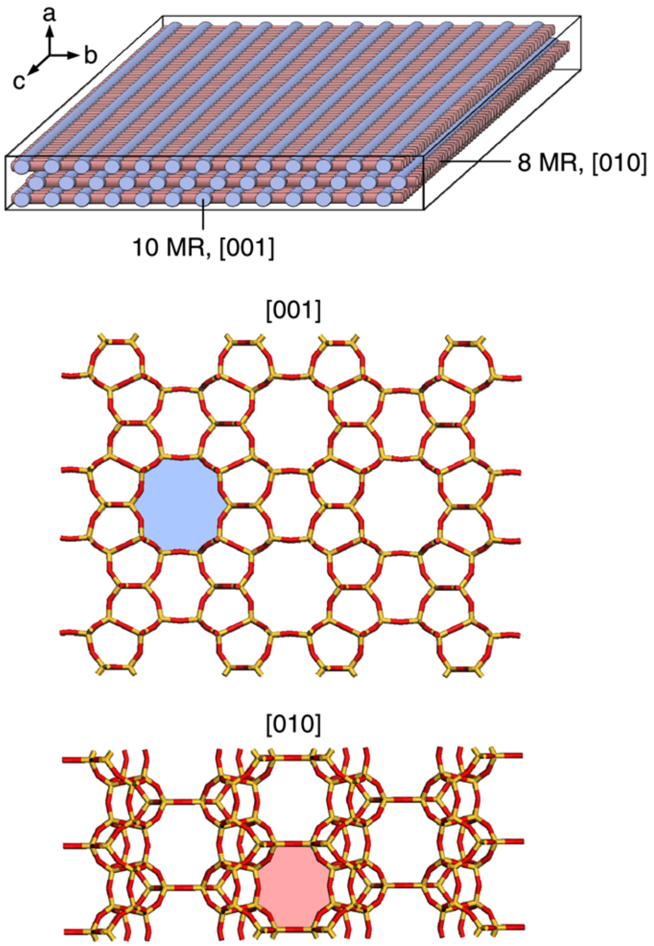

Fig. 1. Structure of ferrierite in the [0 0 1] and [0 1 0] directions. The openings of the 10-MR and 8-MR pores are colored.

Strategies for the latter purpose comprise the preparation of delaminated zeolites [27], zeolite nanocrystals [28], composites of zeolites and ordered mesoporous materials [29], and mesoporous zeolite crystals [30]. To date, the only demonstrated way to enhance the accessibility of ferrierite consists in delaminating the lamellar PREFER precursor [31]. This treatment leads to ITQ-6, a nanosheet-based non-microporous material with an external surface area of 600 $m^2\,g^{-1}$. This route requires a less conventional template to synthesize PREFER (4-amino-2,2,6,6-tetramethylpiperidine) and an ionic surfactant (cetyltrimethylammonium bromide) as a swelling agent. In consideration of wide implementation, the use of commercially available ferrierite and cheap reagents is highly desirable. Unfortunately, post-synthesis dealumination by high-temperature calcination, steaming, treatment with HCl, oxalic acid, $(NH_4)_2SiF_6$, or $SiCl_4$ causes no modification of the porous characteristics of ferrierite [8,13,32,33] in contrast to the noticeable effect on other zeolite structures [34].

The selective extraction of framework silicon in aqueous NaOH solutions, known as desilication, is a versatile, effective, and simple approach to generate intracrystalline mesoporosity in ZSM-5 [35,36], ZSM-12 [37], mordenite [38], and beta [39,40] zeolites. As a result, a hierarchical zeolite is obtained, combining the unique catalytic properties of the intrinsic micropores and the facilitated access and improved transport consequence of a complementary mesopore network. Desilication also proved to be suitable to prepare uniform octadecasil nanocrystals with a high external surface area [41]. Preliminary work by some of us [42] showed that ferrierite was also susceptible to extensive mesopore formation by alkaline treatment under relatively harsh conditions (0.5 M NaOH, 348 K, 5 h). However, the increase in mesopore surface area (from 20 to 130 $m^2\,g^{-1}$) was accompanied by a marked decrease in micropore volume (from 0.13 to 0.08 $cm^3\,g^{-1}$) due to the excessive silicon leaching. Accordingly, optimization of the alkaline treatment is required to develop significant mesoporosity while preserving to the largest possible extent the crystallinity and acidity of the original microporous material.

Herein, we have subjected a commercial ferrierite sample (Si/Al = 29) to NaOH treatments in order to generate controlled mesoporosity by selective silicon extraction. The bulk Si/Al ratio of the starting material was the optimal window of 25–50 [43]. The influence of the NaOH concentration, temperature, and time on the porous properties was screened and compared with conventional dealumination post-treatments (steam and acid leaching). Based on detailed characterization, insights into the desilication mechanism and the nature of the introduced porosity are discussed. The catalytic performance of the ferrierite samples was evaluated in the pyrolysis of low-density polyethylene. This application is of practical importance for chemical recycling of plastic waste by transformation into valuable fuels or chemicals [44]. In this classical cracking reaction, purely microporous ferrierite displays a low degradation activity compared to other zeolite types such as beta and ZSM-5 [45]. This was attributed to mass-transfer constraints of the branched polymer to penetrate the relatively small ferrierite micropores. Therefore, it is a suitable model reaction to evaluate the eventual benefit of the introduced secondary mesoporosity on the catalytic performance.

2. Experimental

2.1. Parent zeolite and treatments

A commercial ferrierite from Zeolyst (CP 914, nominal Si/Al = 27, NH_4-form) was used as starting material. The sodium content was <0.004 wt.%. Prior to the characterization and treatments, the as-received sample was calcined in static air at 823 K for 5 h using a heating rate of 5 K min^{-1}. The resulting sample is referred to as the parent zeolite (P).

Alkaline treatments (ATs) of the zeolite were carried out in a 16-parallel reactor system (MultiMax from Mettler Toledo), varying NaOH concentration (0.1–1 M), temperature (333–363 K), and time (0.5–9 h). The reactors (17 mm i.d., total volume 50 cm^3) were filled with 10 cm^3 of NaOH aqueous solution, sealed, and introduced in the reactor block. Once the desired temperature was reached, zeolite powder (330 mg) was added to each reactor and stirred magnetically at 500 rpm. After the treatment, the zeolite suspension was cooled down in an ice-water mixture and filtered. The resulting solids were washed with distilled water until pH neutral and dried at 333 K for 12 h. The filtrates were kept for chemical analysis. Finally, the alkaline-treated samples were brought into the protonic form via three successive exchanges in a 0.1 M NH_4NO_3 aqueous solution at room temperature followed by calcination at 823 K for 5 h.

The parent ferrierite was also treated in steam and acid. Steaming (ST) was carried out using a quartz reactor with a shallow bed of zeolite powder (266 mbar H_2O and 40 cm^3 STP min^{-1} of He flow, 150 mg of zeolite, 873 K, 2.5 h). Treatments in hydrochloric acid (HCl) and oxalic acid (OA) were carried out at the following conditions: (i) 10 cm^3 of 5.25 M HCl aqueous solution, 330 mg of zeolite, 298 K, 4 h and (ii) 10 cm^3 of 0.5 M $H_2C_2O_4$ aqueous solution, 500 mg of zeolite, 343 K, 2 h. The resulting samples were filtered, washed, dried at 333 K, and calcined at 823 K for 5 h.