Template-Free Synthesis of Zeolite Ferrierite and Characterization of its Acid Sites

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Dedicated to Professor Dr. Wolf-Dieter Deckwer on the occasion of his 60th birthday

1 Introduction

Using organic templates in the hydrothermal synthesis of zeolites enables one to broaden the range of accessible n_{Si}/n_{Al} ratios in the products, to enhance their crystallinity, and/or to control the nucleation rate during the synthesis. Moreover, many zeolite structures can only be synthesized, if such structure-directing agents are employed. Nevertheless, whenever it comes to the commercial-scale production of zeolites, there is a high incentive for template-free syntheses, both for ecological and economical reasons.

In 1964, Barrer and Marshall [1] discovered a crystalline, microporous phase during hydrothermal treatment of strontium-containing synthesis gels between 300 °C and 450 °C. This material was called Sr-D and has been assigned to the FER framework type. A more thorough examination of the crystallization fields was carried out by Bellussi and coworkers [2]. The synthesis in the presence of potassium ions was examined in greater depth by Toyo Soda [3] and scaled up for commercial production [4]. In this communication we report on new methods for the template-free synthesis of zeolite ferrierite.

2 Experimental

For the template-free synthesis of ferrierite (code of the International Zeolite Association: FER), 0.83 g of finely cut aluminum ribbon (p.A., Merck) was added to a solution of 2.3 g KOH (p.A., Riedel-de Haën) in 42 g H_2O under vigorous stirring. After about 12 h stirring, the aluminum was completely converted, and a crystalline precipitate was formed. To this mixture, a solution of 1.6 g NaOH (p.A., Merck) in 42 g H_2O was added immediately. After one more hour of stirring, 17.9 g of fumed silica (Cab-osil M5, Fluka) was introduced by kneading the mixture with a stainless steel spatula until it was homogeneous. A gel with the following molar composition was obtained:

18.0 SiO_2 : Al_2O_3 : 1.24 K_2O : 1.21 Na_2O : 280 H_2O

The crystallization was performed at 180 °C in a PTFE-lined stainless-steel autoclave (V = 300 cm^3) under rotation within six days. The product was filtered, rinsed with 2 dm^3 of water, and dried for 10 h at 150 °C.

For comparison, two ZSM-35 samples (FER topology as well) were prepared according to recipes given in a Mobil patent [5] with pyrrolidine or ethylenediamine as templates within six days at 180 °C. The synthesis gels obtained had the following molar compositions:

18.0 SiO_2 : Al_2O_3 : 4.98 Na_2O : 9.41 NaCl : 3.57 SO_3 : 15.9 pyrrolidine : 632 H_2O and 17.7 SiO_2 : Al_2O_3 : 1.86 Na_2O : 23.2 ethylenediamine : 745 H_2O.

The NH_4^+ forms were prepared (after calcination at 600 °C if a template was used) by several ion exchanges with 0.1 mol dm^{-3} aqueous NH_4NO_3 solutions. The zeolites were characterized by X-ray powder diffraction (CuKα radiation, Siemens D5000), scanning electron microscopy (Cambridge CAMSCAN 44), elemental analysis by AES/ICP (Perkin-Elmer Plasma 400), nitrogen adsorption at –170 °C after activation at 450 °C *in vacuo* for 12 h (Micromeritics ASAP 2050), MAS NMR spectroscopy (Bruker MSL 400), and FTIR spectroscopy (Bruker Vector 22) after activation at 400 °C.

3 Results and Discussion

Besides metallic aluminum, several other aluminum sources were tested, yet none of these alternatives enabled the template-free synthesis of ferrierite: if aluminum sulfate (p.A., Riedel-de Haën), aluminum nitrate (p.A., Riedel-de Haën) or aluminum triisopropylate (synthesis grade, Merck) were used, no crystalline solid precipitated. Aluminum hydroxide (p.A., Fluka), pseudo-boehmite (Pural SB, Condea), and aluminum oxide (Alumina, Woellm Pharma) were not converted at all. As silicon sources, fumed silica (Cab-osil M5, Fluka) and colloidal silica sol (Bayer Levasil VPAC 4039, 30 wt.-% SiO_2) could be employed, whereas tetraethyl orthosilicate (purum, Merck) yielded α-quartz exclusively, even with decreased synthesis time.

In further experiments, synthesis gels with different aluminum contents were prepared according to the aforementioned method, keeping the sum of n_{Si} and n_{Al} constant. Samples of pure zeolite ferrierite were only obtained with aluminum contents $n_{Al}/(n_{Si}+n_{Al})$ in the gel between 0.123 and 0.100 (corresponding to n_{Si}/n_{Al} ratios between 7.1 and 9.0). With decreasing aluminum content, the formation of α-quartz as a by-product increased. With increasing aluminum content, a second phase (heulandite, code of the International Zeolite Association: HEU; cf. Fig. 1) and finally amorphous products were produced. The product with the highest crystallinity was obtained with an aluminum content of 0.100 (n_{Si}/n_{Al} = 9.0) in the gel. The aluminum contents of the products were between 0.132 and 0.114 (n_{Si}/n_{Al} ratios between 6.6 and 7.8; cf. Tab. 1). Potassium-free synthesis gels (KOH was replaced by an equimolar amount of NaOH) resulted in amorphous products. From this it is concluded that potassium ions have a structure-

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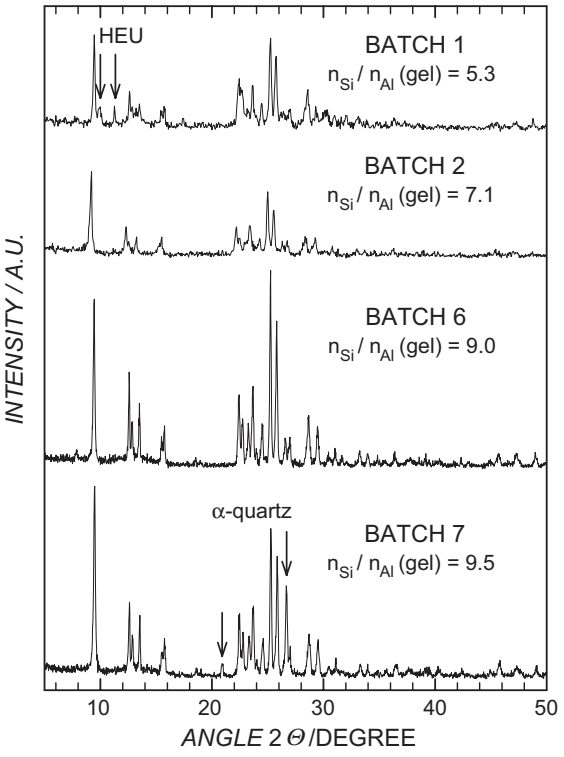

Figure 1. X-ray powder diffraction patterns of selected ferrierite samples (see also Table 1). Reflexes due to impurities are indicated by arrows (HEU = heulandite).

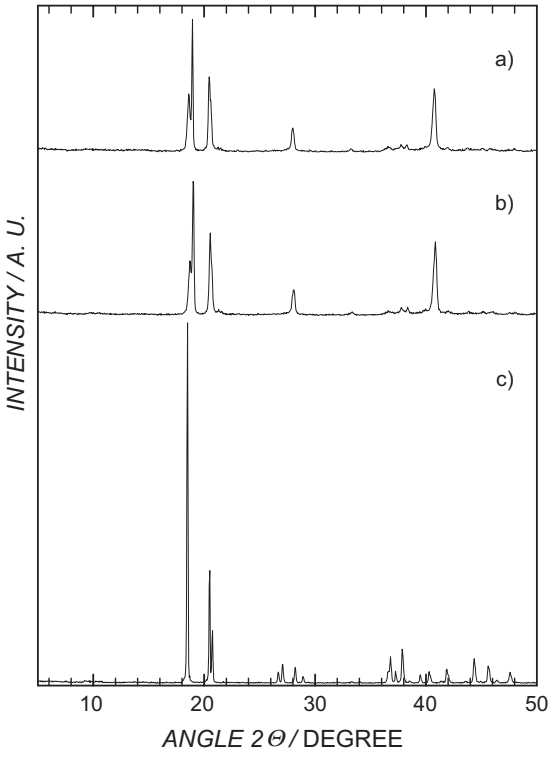

Figure 2. X-ray powder diffraction patterns of precipitates after the first synthesis step (a), after the second step (b), and of commercially available aluminum hydroxide (Fluka, c).

directing effect. This result is supported by the analyses of the products: Synthesis gels with n_K/n_{Na} ratios of 1 yielded n_K/n_{Na} ratios of about 6.0 in the product, indicating that potassium ions are preferentially built into the structure.

Further experiments were carried out in order to examine the crystallization process: The precipitate formed in the first synthesis step (cf. Section 2) was separated, rinsed with acetone and dried at 60 °C. The X-ray powder diffraction pattern of this species is similar to that of aluminum hydroxide (cf. Fig. 2). Even after addition of the sodium hydroxide solution, the precipitate did not dissolve (cf. Fig. 2b), suggesting that this species is only consumed during the crystallization step, thus keeping the amount of the accessible aluminum in the synthesis gel relatively low. Adding the complete amount of KOH and NaOH in the first synthesis step resulted in a clear solution. Whereas ferrierite was obtained with an n_{Si}/n_{Al} ratio of 9.0 in the gel with this method, a n_{Si}/n_{Al} ratio of 7.1 gave only amorphous products. Therefore, the aluminum content in the gel must be kept below a critical level if ferrierite is to form. At this stage of the investigation, we interpret the results as follows: The aluminum hydroxide precipitate seems to be an aluminum reservoir. Thus, the amount of accessible aluminum in the synthesis gel is ideal for the nucleation of ferrierite, and the production of nuclei of other phases is suppressed. During the synthesis, the aluminum for the crystal growth is delivered gradually.

Zeolite ferrierite synthesized in this way without a template was characterized in some detail and compared to zeolite ZSM-35 synthesized via the more conventional routes with a template. Scanning electron microscopy indicated an orthorhombic flat-prismatic morphology typical of zeolite ferrierite. While the crystals synthesized with pyrrolidine as template were *ca*. 6 μm in size, the crystals obtained without organic templates had a size of only *ca*. 1 μm. With ethylenediamine as structure-directing agent, crystals with a diameter significantly below 1 μm and with a nearly hypidiomorphic shape were obtained.

Sorption isotherms using nitrogen as an adsorptive showed that the maximum loading of unmodified ferrierite synthesized with-

Table 1. Compositions of the synthesis gels and the products (FER = ferrierite; HEU = heulandite).

batch	n_S/n_{Al} (gel)	product	n_S/n_{Al} (product)	n_K/n_{Al} (product)	n_{Na}/n_{Al} (product)
1	5.3	FER + HEU	5.1	0.70	0.35
2	7.1	FER	6.7	0.85	0.15
3	7.5	FER	6.6	0.82	0.17
4	7.9	FER	7.1	0.84	0.14
5	8.0	FER	6.9	0.88	0.15
6	9.0	FER	7.8	0.85	0.11
7	9.5	FER + α-quartz	8.4	0.87	0.12

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out a template (batch No. 6, cf. Tab. 1) was low, viz. 18 $cm^3\ g^{-1}$. Obviously, the potassium cations require significant space within the pores. After ammonium ion exchange and calcination to obtain the protonated form, the maximum loading increases drastically to 106 $cm^3\ g^{-1}$, which is very close to the sorption results on a ZSM-35 sample synthesized with pyrrolidine as template (maximum loading: 103 $cm^3\ g^{-1}$).

The ^{29}Si MAS NMR spectrum of the ferrierite sample synthesized without a template (batch 2) showed peaks at $\delta = -106$ ppm, $\delta = -110$ ppm, and $\delta = -115$ ppm, which partially overlapped. In the ^{27}Al MAS NMR spectrum, only a single peak at $\delta = 53.9$ ppm was observed, which is indicative of tetrahedrally coordinated framework aluminum. No peak was observed at $\delta = 0$ ppm, hence, the presence of octrahedrally coordinated extra-framework aluminum can be excluded.

Fig. 3 shows the FTIR spectra of zeolite ferrierite synthesized without a template after activation and adsorption of pyridine. Obviously, the intensity of the band at 3600 cm^{-1} caused by the Brønsted acid Si(OH)Al groups is dependent on the sorption temperature of pyridine. In Fig. 4, the integral of the band caused by pyridine molecules interacting with acid Si(OH)Al groups (1545 cm^{-1}), referenced to a uniform density, is plotted as a function of the temperature. The integral absorption of this band increases with increasing temperature up to 400 °C, whereupon it starts to decrease due to the desorption of pyridine at temperatures above 400 °C. In comparison to the two samples synthesized with templates, ferrierite synthesized without a template possesses the largest number of acid sites accessible to pyridine molecules [6–8].

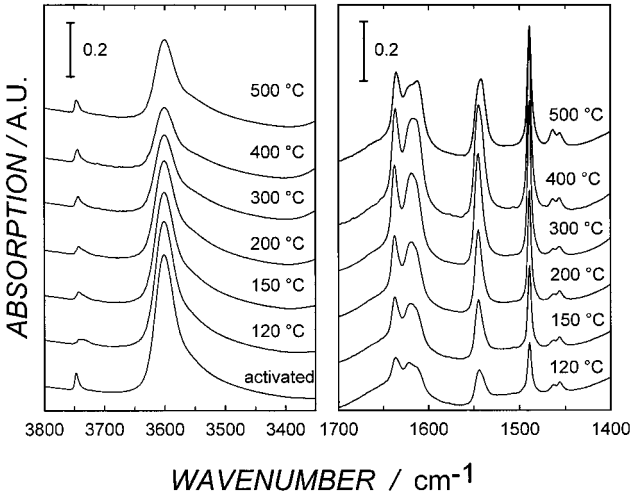

Figure 3. FTIR spectra of zeolite ferrierite synthesized without any organic template after activation (on the left) and after sorption of pyridine at different temperatures (on the right).

In conclusion, zeolite ferrierite can be synthesized without a template. The sample quality compares well with the one of ferrierite samples synthesized in the conventional manner using organic templates. Ferrierite synthesized by the procedure disclosed here possesses an interesting distribution of acid sites, as found by the pyridine adsorption experiments.

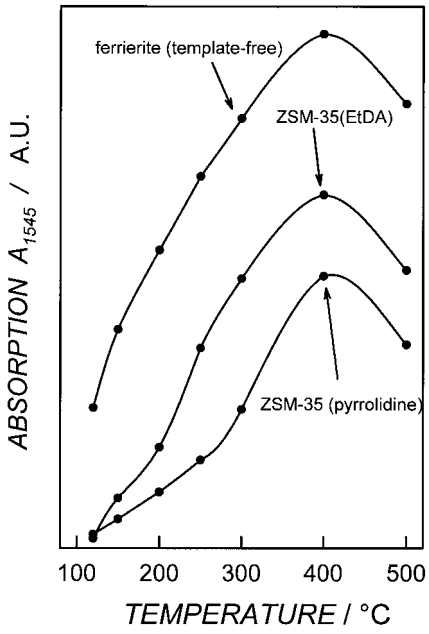

Figure 4. Integral absorption of the band at 1545 cm^{-1} (pyridine adsorbed on a Brønsted acid site) at different temperatures.

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