

Direct hydrothermal conversion of high-silica faujasite and zeolite β to ZSM-5 and its catalytic performance

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In the absence of a structure-directing organic molecule, aluminosilicate ZSM-5 is produced directly from high-silica zeolite Y or zeolite β by a simple hydrothermal treatment of the alkali metal hydroxide-treated starting zeolite material. NMR and FTIR results clearly suggest that the majority of the Al(III) species is present in the framework yielding Brønsted acid sites. Addition of an appropriate organic molecule such as tetrapropylammonium bromide or tetrabutylammonium bromide facilitates the formation of ZSM-5 and ZSM-11, respectively. The protonated form of all the ZSM-5 catalysts shows very good catalytic activity for the conversion of methanol to hydrocarbon.

KEY WORDS: high-silica faujasite; zeolite β ; hydrothermal conversion; ZSM-5.

1. Introduction

Open-framework structured aluminosilicates, titanosilicates, silicoaluminophosphates and transition metal ion-substituted aluminophosphates have found a variety of novel applications over the last two decades [1–15]. By fine tuning the chemical composition, it is possible to design and synthesize several environmentally benign microporous catalysts that avoid the use of highly corrosive reagents, minimize the formation of side (waste) products and more importantly promote highly shape-selective reactions. The most challenging step in producing these materials is the synthesis of a microporous solid with a specific structure for a given catalytic application. For example, the choice of chemical composition to yield the optimum number (not necessarily large) of catalytic sites and necessary pore dimensions for shape-selective reaction are some of the essential factors that should be considered for a specific catalytic application. Although a number of synthetic approaches for the production of microporous aluminosilicates have been reported since the early work by Barrer [16], one of the most common approaches in the last decade is the use of an organic template molecule, preferably an amine or a quaternary ammonium hydroxide as the structure-directing agent (SDA) [2,17]. In addition, in a few recent studies, zeolites were also used as the source for silica or alumina to produce other microporous architectures with the aid of an organic SDA [2,17] and, furthermore, it was also shown that certain

aluminosilicates such as zeolite Y or zeolite A transform to other microporous (without the presence of an SDA) aluminosilicates, but these examples were restricted to low-silica materials [18]. Although the use of these organics have certain advantages, considerable effort has been directed toward the synthesis of microporous solids without the use of organic template molecules to reduce the production costs and to avoid the release of toxic carbon or nitrogen products, created when the templated microporous materials are subjected to heat treatment, in air, to remove the occluded organic species from the zeolitic pores. A number of zeolites (*e.g.*, zeolite A, zeolite Y or X or chabazite) have been successfully prepared without using any structure-directing organic templates [16,19–21].

Amongst the various microporous aluminosilicates, ZSM-5 has found an important role in many shape-selective reactions, since this material is the most acidic in the aluminosilicate family of catalytic materials [22]. The most commonly employed procedure for preparing aluminum- (or titanium)-containing materials with an MFI structure is by subjecting a gel mixture containing appropriate amounts of aluminum oxide, silicon oxide and more importantly tetrapropylammonium hydroxide as the SDA [23]; there have been few reports that deal with the preparation of ZSM-5 without the use of an organic agent [24–27]. Here we describe the production of ZSM-5 without the aid of an SDA, which we achieved by the use of commercially available zeolite Y or zeolite β (as the silicon and aluminum source), which were subjected to hydrothermal treatment after reaction with sodium hydroxide solution.

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2. Experimental

In a typical synthesis of ZSM-5, 1 g of zeolite Y or zeolite β having an Si/Al ratio of *ca.* 80 (in the case of zeolite β , an Si/Al ratio of 300 was also used) was reacted with a 0.3 M solution of NaOH. Both zeolite Y and zeolite β were obtained from ZEOLYST International (USA). In the non-templated synthesis procedure, the resulting mixture was stirred for *ca.* 1 h before being transferred to a Teflon-lined autoclave for hydrothermal treatment at 150 °C for about 24 h. For the templated synthesis procedure, the above mixture was reacted with 0.21 g of tetrapropylammonium bromide (TPABr) before subjecting it for hydrothermal treatment at 175 °C for *ca.* 24 h. For the ZSM-11 synthesis, tetrabutylammonium bromide (TBABr) was used as the SDA and similar hydrothermal conditions to those used for ZSM-5 were employed. The phase purity of all the solids extracted from the hydrothermal synthesis was examined with a Siemens D500 X-ray diffractometer equipped with a $\text{CuK}\alpha$ source.

All the as-prepared ZSM-5 samples were calcined and ion exchanged three times with 1 M ammonium chloride. The ammonium form of all the samples was calcined in air to obtain the proton form and these solids were examined using the solid-state NMR technique. NMR

spectra were recorded using AMX600 and MSL300 instruments for ^{27}Al solid state and ^{29}Si solid state, respectively. *In situ* FTIR spectra were recorded using a Matteson Infinity spectrometer equipped with an MCT detector. This equipment has a diffuse reflectance attachment and a COLLECTOR from SpectraTech, which was used to record the spectra.

Catalytic reaction of methanol over ZSM-5 catalyst was carried out using a custom-built continuous-flow reactor. In a typical experiment, 200 mg of the protonated form of the ZSM-5 catalyst were pelletized, then crushed using a 20 μm mesh sieve prior to being loaded into a quartz reactor tube. The sample was heated to 300 °C in flow of nitrogen before introducing methanol injected at a fixed flow rate of 0.05 ml/min using a syringe pump. The products were analyzed using a Porapak N column in a Perkin-Elmer 3010 gas chromatograph equipped with a flame ionization detector.

3. Results and discussion

We noticed first, in the non-templated synthesis procedure, that the starting zeolite material dissolves in NaOH solution forming a slightly turbid mixture. The XRD pattern (see figure 1) of the solid extracted after a

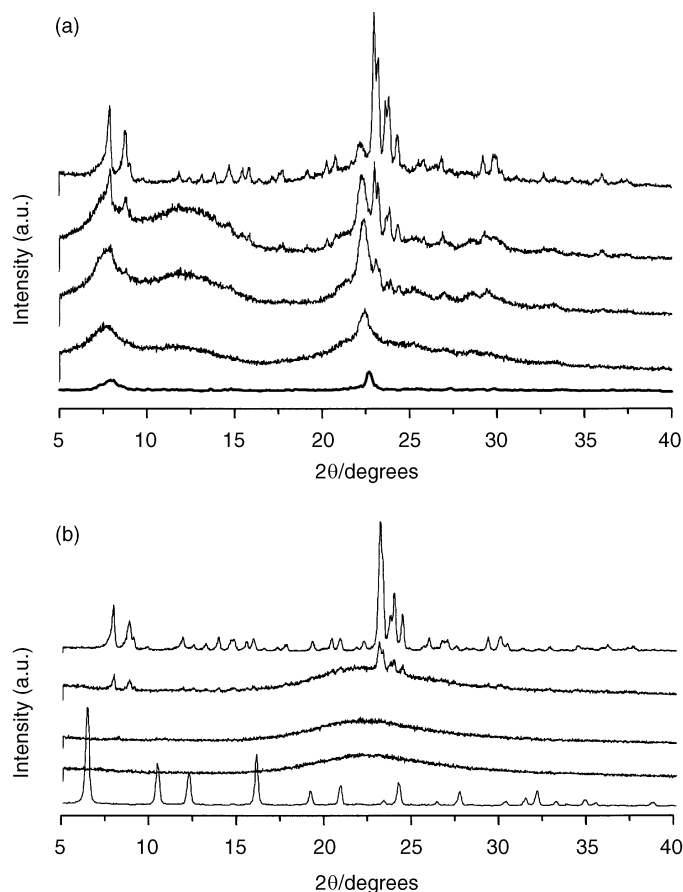


Figure 1. XRD patterns recorded for the samples extracted after hydrothermal treatment for a specific period of time. The sequence for the formation of ZSM-5 from zeolite β is shown in (a) and that from zeolite Y is given in (b).

few hours (between 4 and 8 h) showed that there were no crystalline phases present in the solid related to either the starting zeolitic material or any other intermediate product. Crystalline ZSM-5 material could be extracted after *ca.* 24 h of hydrothermal treatment and the yield increased with time. However, prolonged (beyond 36 h) hydrothermal treatment or at elevated temperature (above 150 °C) resulted in the further conversion of ZSM-5 to dense phases such as tridymite or quartz. The entire XRD sequence investigated by extracting the solid after hydrothermal treatment for specific period is given in figure 1.

In a separate experiment, we mixed appropriate amounts of the SDA to the turbid solution of zeolite Y

or β dissolved in NaOH, before introducing the solution into the Teflon-lined autoclaves and subjecting them to hydrothermal conditions. Highly crystalline ZSM-5 or ZSM-11 materials were extracted when TPABr or TBABr, respectively, was added to a mixture of the starting zeolite in the alkaline solution and after hydrothermal treatment for 24 h at 150 °C. It should be noted that by using the high-silica form of zeolite Y or β , it was *not* necessary to add excess silica to the gel mixture, whereas when low-silica zeolite Y was used as starting material, it was found that additional amounts of silica were necessary to form ZSM-5 or ZSM-11 [28]. It is also interesting that when tetraethylammonium hydroxide (TEAOH) was used as the SDA (typical

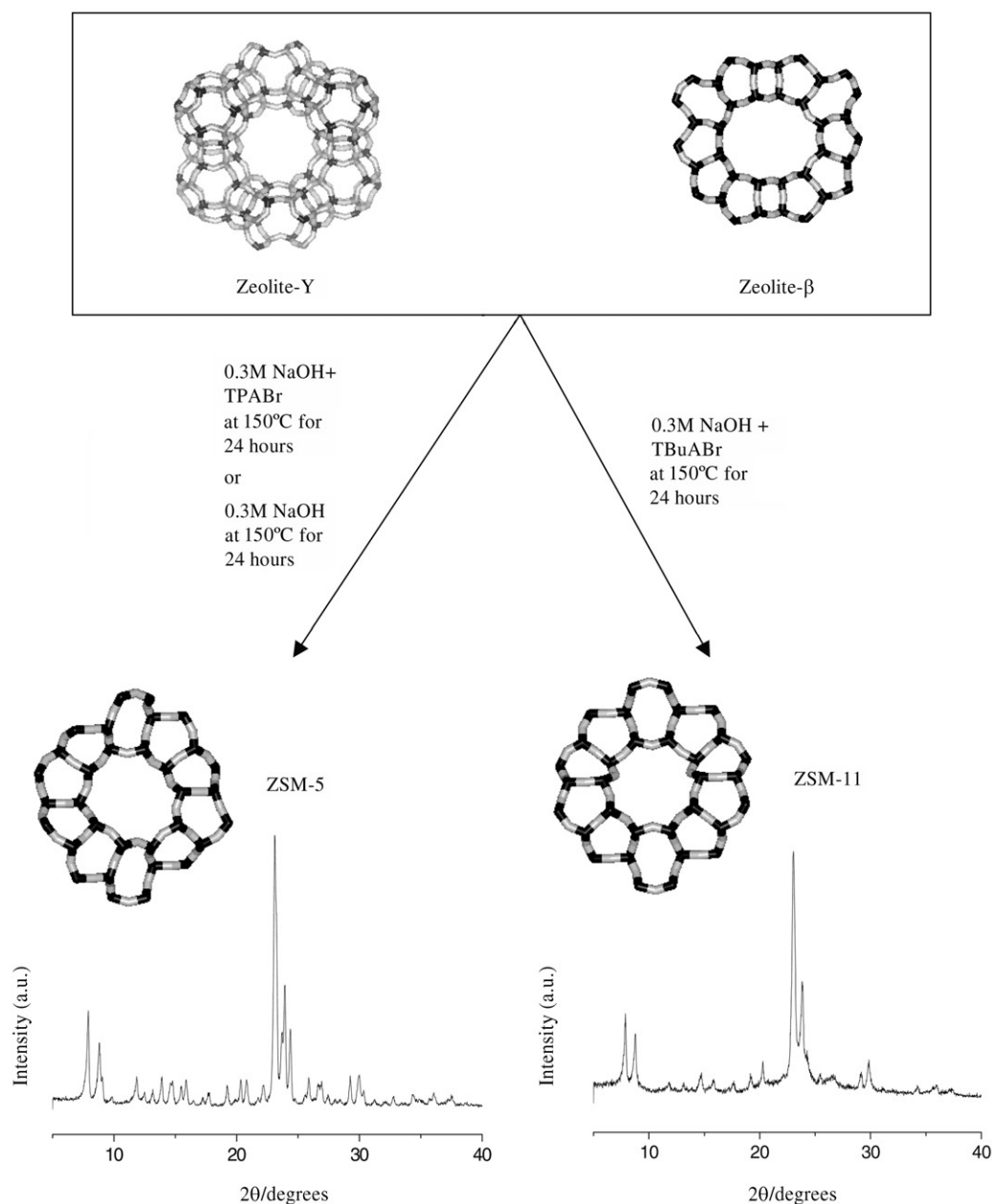


Figure 2. Schematic summary of the preparation of ZMS-5 and ZSM-11 from zeolite Y and zeolite β . The XRD patterns shown clearly demonstrate that phase pure materials were prepared irrespective of whether we used a structure-directing agent or not.

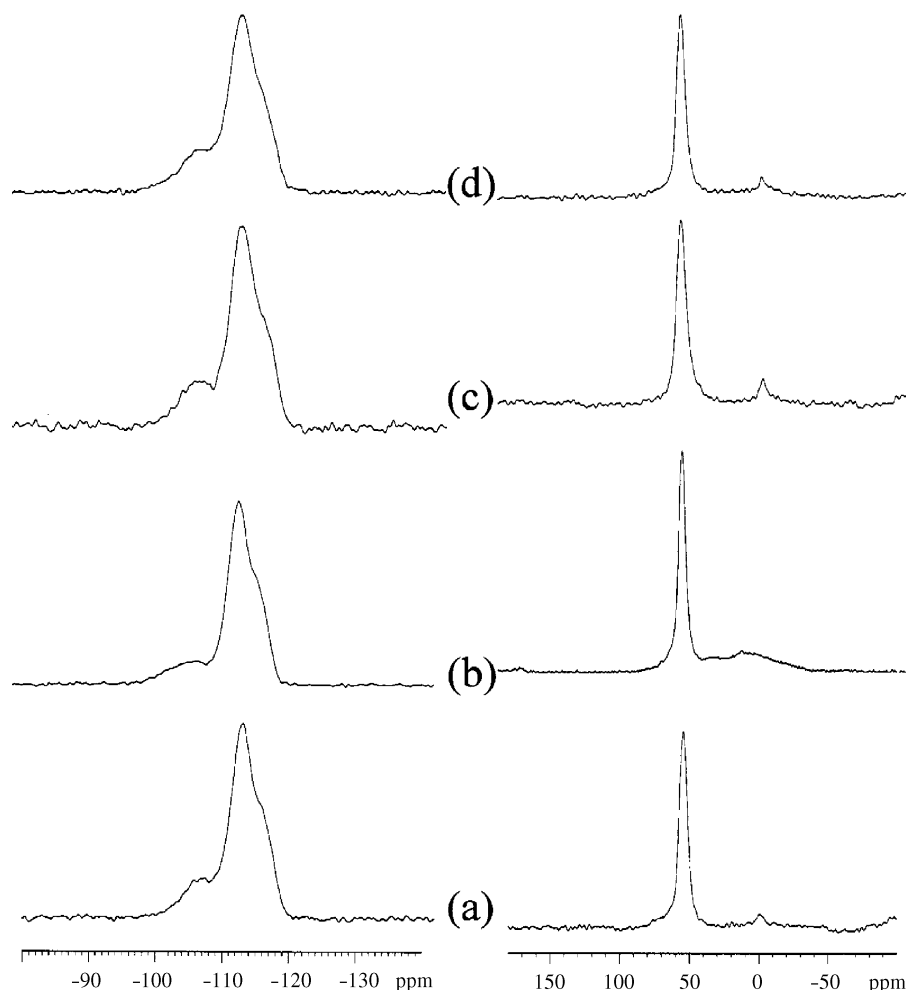


Figure 3. ^{29}Si (left) and ^{27}Al (right) MAS NMR spectra of the protonated form of the ZSM-5 materials prepared employing various conditions and starting materials. From bottom to top: (a) ZSM-5 from H-zeolite- β (Si/Al = 75) and TPABr; (b) ZSM-5 from H-zeolite-Y (Si/Al = 80) and TPABr; (c) ZSM-5 from H-zeolite- β (Si/Al = 75); (d) ZSM-5 from H-zeolite-Y (Si/Al = 80).

structure-directing agent used for the synthesis of zeolite β , zeolite β was produced only when we used the well-established procedure [23] for the synthesis of zeolite β . The various conditions employed in this work for the preparation of ZSM-5 and ZSM-11 are summarized in figure 2.

A detailed NMR study was undertaken to determine the silicon and aluminum environment in both the initial solution (starting zeolite material dissolved in NaOH) and the final solid obtained from both the templated and non-templated synthesis procedure. The solution ^{29}Si NMR results show clearly the presence of Q, Q1, Q2 and Q3 species [29], suggesting that there appears to be complete dissolution of the starting crystalline zeolite. In figure 3 we show the ^{29}Si and ^{27}Al NMR spectra of the various ZSM-5 materials (converted to proton form) prepared by different methods. Although we do not see appreciable differences in the spectra of the various materials with a majority of the Al(III) ions present in a tetrahedral environment, it is interesting that, after converting the ZSM-5 materials to the H

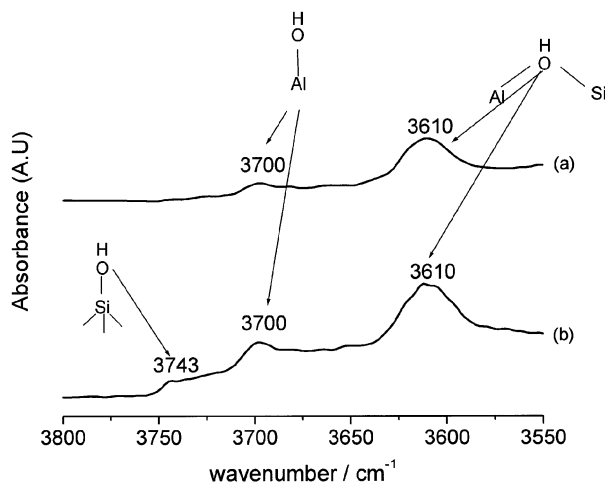


Figure 4. IR spectra of the dehydrated, protonated form of ZSM-5 prepared without the aid of an organic template: (a) from zeolite β (Si/Al = 75) and (b) from zeolite Y (Si/Al = 80).

Table 1

Summary of the typical catalytic conversion of methanol over ZSM-5, prepared using zeolite Y and zeolite β as the starting material and without the aid of organic template

Product	ZSM-5 from zeolite Y	ZSM-5 from zeolite β
% conversion of methanol	97.26	95.74
Dimethyl ether	1.59	0.04
CH ₄	1.23	0.97
C ₂ H ₄	27.94	22.30
C ₂ H ₆	0.42	0.20
C ₃ H ₆	28.03	29.14
C ₄ H ₈	10.39	13.10
C ₄ H ₁₀	4.08	5.34
C ₅ H ₁₀	2.09	2.48
C ₅ H ₁₂	3.68	4.74
C ₆₊	20.55	21.69

The reaction was conducted at 573 K using 200 mg of ZSM-5. Nitrogen flow was maintained at 60 ml/min. The WHSV was 10.0. Methanol was fed using a syringe pump at a constant infusion rate of 0.05 ml/min.

form, a slight decrease in the ^{29}Si resonance (*ca.* –107 ppm) associated with silicon having one aluminum neighbor and a corresponding increase in the signal associated with that for an octahedral Al(III) species in ^{27}Al NMR spectra (*ca.* 0 ppm) were observed. However, *in situ* IR data (see figure 4) clearly show the presence of Brønsted acid sites, as seen by the intense band at *ca.* 3610 cm^{–1} characteristic of the OH stretching frequency associated with the Si–O–Al bridges. This bridging hydroxyl band is seen in all the transformed, protonated zeolites, in particular for the ZSM-5 prepared without the use of an organic template molecule. This indicates that strong acid sites are present in these materials.

To confirm that the ZSM-5 produced by this novel direct conversion from high-silica zeolite is a good solid acid catalyst, we carried out a systematic study of methanol dehydration over this catalyst and the results are given in table 1. It is clear that the ZSM-5 produced by this new method, irrespective of the starting zeolite source, converts methanol very efficiently to olefins and hydrocarbons when the reactor is operated at *ca.* 300 °C. This is not only consistent with the data reported in the literature [22], but also clearly supports the *in situ* FTIR (see figure 4) finding that strong acid sites are present in these ZSM-5 catalysts.

In summary, the results of the present study clearly show that by an appropriate choice of Si/Al ratio, it is possible to prepare ZSM-5 without the aid of either seeding or templating agents, a novel approach which is likely to be useful for the production of zeolitic membranes and environmentally benign catalytic materials.

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