Synthesis and Characterization of ZSM-5 Zeolite from Amorphous Sodium Aluminosilicate Dry Gel

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ZSM-5 zeolite was synthesized from an amorphous sodium aluminosilicate dry gel using hydrothermal method, in the presence of tetrpropylammonium hydroxide (TPAOH) as a template. Prepared samples of different forms of ZSM-5 zeolite have been characterized by X-ray diffraction (XRD), Fourier Transformed-Infrared Red (FT-IR) and scanning electron microscopy (SEM) analysis. XRD patterns show that the synthesized zeolite has a typical MFI framework. FT-IR spectra confirm the production of ZSM-5 type zeolite by the characteristic band of five-membered ring of pentasil structure (double ring vibration) at 540.90 cm⁻¹. Scanning electron microscope revealed that the crystals have a cauliflower-like morphology, which characterizes a ZSM-5 zeolite synthesized with quaternary ammonium cation TPA⁺.

Keywords: aluminosilicates, ZSM-5 zeolite, tetrpropylammonium hydroxide

There are numerous reports on the synthesis of zeolites with different alumina and silica sources and different types of structure-directing agents, in various conditions. For example, Ingram et al. [1] synthesized a HZSM-5 zeolite from a sodium silicate and aluminium sulphate, using tetrpropylammonium bromide as template at 393 K for 24 h, followed by 443 K for 30 h. Kulkarni et al. [2] reported synthesis of highly crystalline ZSM-5 from sodium aluminate and tetraethylorthosilicate (TEOS) using an autoclaving time of 4-6 h with various solvents under high pressures (40-60 atm) and temperatures (503-523 K). It was synthesized MCM-41/ZSM-5 by crystallization of aged gels in the presence of cetyltrimethylammonium cations [3]. Makarfi et al. [4] prepared a ZSM-5 based catalyst by adding at the crystallization stage spirit fraction, X-oils and hexamethyl-enediammine as structural units. Crystallization was carried out at a constant temperature of 448 K for a period of six days. The researchers reported synthesis of micro-mesoporous ZSM-5 by using carbon black Carbon Black Pearl 2000 as a secondary template to tetrpropylammonium hydroxide (TPAOH) [5]. Koo et al. [6] also used TPAOH as a template for ZSM-5 and Carbon Black Pearls 2000 as a hard template. Carbon nanoparticles were simply mixed into synthesis precursors of ZSM-5 and hydrothermally treated by microwave irradiation for 1 hour. Hu et al. [7] proposed a microwave-assisted two-step hydrothermal procedure to prepare various zeolites (e.g. silicalite-1, ZSM-5, LTL, BEA and LTA). The precursor sols were stirred continuously at room temperature for 48-72 h before they were hydrothermal treated under microwave irradiation for 2 h. This recently developed microwave synthesis could dramatically shorten the synthesis time, but the difficulty in designing and handling of microwave reactor is a big problem for the large-scale synthesis [8].

In this paper, we report the hydrothermal synthesis of H-ZSM-5 zeolite prepared by a two-step route: (i) preparation of an amorphous sodium aluminosilicate dry gel by precipitation and drying and (ii) hydrothermal synthesis. The synthesis of the zeolite was performed in the presence of tetrpropylammonium hydroxide as template, for 48 h which is a relatively low crystallization time in comparison with previous literature works (e.g. 3-7 days) [1, 4].

Experimental part

The synthesis of the ZSM-5 zeolite

Raw materials used for the preparation of the ZSM-5 zeolite were the following: sodium silicate as silica and sodium sources (Merck, 28% SiO₂, 8.6% Na₂O) and aluminum nitrate (NH₄NO₃) solution for two times at 363 K followed by precipitation at a pH value of 7.0-7.5. The resulting gel has been processed by filtering, drying at 353 K and ball mill grinding, respectively to obtain a fine powder of amorphous sodium aluminosilicate gel. The synthesis mixture was prepared by adding the organic template to the aqueous suspension of sodium aluminosilicate dry gel under stirring. The resulting mixture had a pH value around 13.5 and the following molar composition: SiO₂ : Al₂O₃ : Na₂O : TPAOH : H₂O = 90 : 1 : 7.07 : 4.5 : 2462. The hydrothermal synthesis has been carried out into 1000 mL stainless steel autoclave equipped with a temperature controller in the following conditions: temperature - 443 K, pressure - 6 bar and time - 48 h, under continuous stirring (150 rpm). The solid product was recovered by filtration, washed with distilled water until the pH reached 7.0-8.0 and dried at 353 K for 8 h. The as-synthesized Na-ZSM-5 zeolite powder was calcined in air at 853 K for 8 h using a heating rate of 2°/min. to decompose and remove organic cations occluded in the zeolite framework. Then, the calcined Na-ZSM-5 zeolite powder was converted to ammonium form by ion exchange with 1M ammonium nitrate (NH₄NO₃) solution for two times at 363 K followed by filtering, washing with distilled water and drying at 353 K overnight. The resulting NH₄-ZSM-5 zeolite powder was used to prepare the formulated zeolite sample.

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The preparation of the formulated ZSM-5 zeolite

The NH₄-ZSM-5 zeolite powder obtained as described above was formulated by extrusion using a pseudo-boehmite type hydrated alumina (65% Al₂O₃) as binder and nitric acid (12 wt. % HNO₃) as peptising agent. The obtained extrudates were dried at room temperature for 24 h and at 353 K overnight and finally calcined at 823 K for 4 h to convert the ammonium form to the hydrogen form of the ZSM-5 zeolite and to transform the hydrated alumina to the γ-Al₂O₃ phase. The final composition of the calcined H-ZSM-5 extrudates consisted of 60 wt. % of H-ZSM-5 zeolite (SiO₂/Al₂O₃ molar ratio = 90/1) and 40 wt. % of γ-Al₂O₃ [9].

Characterization techniques

X-ray diffraction (XRD) of the zeolite samples resulted in different processing stages were recorded on a Bruker Discovery 8 powder diffraction system (0.154 nm, 40 kV, 40 mA) using CuKα radiation in the 20 range of 5-50°. The IR spectra of the formulated H-ZSM-5 were recorded using a Bruker Vertex 70 (ATR) transform infrared spectrometer with germanium crystal at 4000-375 cm⁻¹ intensity, with 4 cm⁻¹ resolution, 16 scans. The measurements were recorded at the room temperature. The zeolite samples were also characterized by scanning electron microscopy (SEM) using a Hitachi S-3400N type II microscope operated at 25 kV.

Results and discussions

XRD analysis

XRD patterns in figure 1 show that the zeolite synthesized as described above has a typical MFI framework and 20 values = 7.9; 8.8; 23; 23.9 degrees that are in agreement with literature [10]. Generally, in all investigated ZSM-5 samples, diffraction peaks are situated in the same positions but some modification in their intensities could be related to different processing treatments conducting to some changes in cationic composition of the zeolite structure. It is evident that a highly crystalline ZSM-5 zeolite has been obtained corresponding to the ZSM-5 (a) sample (fig. 1) that indicates the tetrapropylammonium cation (TPA⁺) can be defined as a true structure directing agent in high silica ZSM-5 synthesis [10, 11]. Comparing XRD patterns of ZSM-5 (a) and ZSM-5 (b), respectively (fig. 1) could be observed decreasing the intensity of the diffraction maxima at low angles after calcination as a result of the elimination of the organic molecules occluded in zeolite channels during the crystallization step. The partial loss of crystallinity upon TPA⁺ removal can be explained by a strong interaction of the organic cation with the negative charge of the aluminosilicate framework (TPA⁺ interaction with tetrahedral AlO₄) [12]. The tetrapropylammonium cation TPA⁺ is located at the channels intersections with the propyl chains extending into both the linear and sinusoidal channels [13]. The tetrapropylammonium hydroxide molecules are responsible for the formation of the microporous structure of MFI type. Pure tetrapropylammonium hydroxide (TPAOH) easily decomposes at temperatures lower 523 K, while the tetrapropylammonium cation (TPA⁺) occluded in the zeolite channels system is removed by calcination at high temperature (> 800 K). When the TPAOH molecules are occluded in zeolites cavities, their decomposition temperature is much higher because of diffusion restrictions and of interactions with the aluminosilicate tetrahedral framework [12].

Lower intensities of the diffraction maxima at low angles appeared after the zeolite has been diluted with 40% Al₂O₃, as can be seen by comparing formulated H-ZSM-5 with powder H-ZSM-5 sample in figure 1. This result could be related to the presence of some material in zeolite channels as extra framework species.

FT-IR analysis

The IR spectra for HZSM-5 zeolite with quaternary ammonium cation TPA⁺ are shown in figure 2. HZSM-5 exhibited absorption bands at 3373.84 cm⁻¹ and 1600 cm⁻¹ attributed to the stretching vibrations of terminal Si-OH groups and adsorbed water molecules. The bands at 1033.98 cm⁻¹ and 790 cm⁻¹ were related to the zeolite framework, i.e. the asymmetric and symmetric flexural vibration of T-O-T (T=Si, Al) groups. The distinct vibration band at 540.49 cm⁻¹ was assigned to the asymmetric stretching mode of the double-five ring in ZSM-5. The band at 431.10 cm⁻¹ was due to the tetrahedral Si-O bending mode. Asymmetric stretching vibration of T-O bond at 1224.56 cm⁻¹ could be assigned to external linkages between TO₄ tetrahedrals. The FTIR spectra of HZSM-5 are in a good agreement with published literature [1, 14].

SEM analysis

The SEM image in figure 3 shows the zeolite sample synthesized with TPA⁺ is well-crystallized and no amorphous materials or other crystalline phases have been obtained. This result is in accordance with X-ray diffraction data. It can see that the crystals have a cauliflower-like morphology, which characterizes a ZSM-5 zeolite synthesized with quaternary ammonium cation TPA⁺. A quite homogeneous size distribution of the individual crystals in figure 3 could be observed. The SEM image of the zeolite processed by extrusion and calcination shows a compacted structure and no ZSM-5 like-morphology but
tiny granules could be observed (fig. 4). It indicates that the ZSM-5 zeolite crystals have been enwrapped by the alumina binder during the formulating process.

Conclusions
A highly crystalline ZSM-5 zeolite exhibiting a MFI type framework has been obtained by hydrothermal crystallization, in relatively low crystallization time, using an amorphous sodium aluminosilicate dry gel with SiO_2/Al_2O_3 molar ratio around of 90 and tetrapropylammonium (TPA^+) cation as a structure directing agent. Using the solid amorphous gel as aluminosilicate crystalline precursor is an advantageous route for ZSM-5 crystallization process yield as compared to homogeneous solutions crystallization route. The powder zeolite has been formulated by extrusion using an alumina binder. X-ray diffraction and scanning electron microscopy have been used to characterize H-ZSM-5 precursors as well H-ZSM-5 based extrudates. Processing the powder zeolite into extrudate form appears as a convenient experimental approach to prepare H-ZSM-5 based catalysts to be used in fixed bed catalytic processes. The catalytic properties of prepared catalysts will be investigated in bioethanol conversion reaction to light hydrocarbons.

References

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