Preparation and Characterization of Nanosized ZSM-5 Zeolite Using Kaolin and Investigation of Kaolin Content, Crystallization Time and Temperature Changes on the Size and Crystallinity of Products

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Nano sized ZSM-5 zeolite samples were synthesized successively from kaolin clay as alumina source having a large amount of quartz (39%) and silicic acid as silica source by hydrothermal treatment with NaOH in the presence of tetrapropylammonium hydroxide as a template. Then the effect of kaolin content, crystallization temperature and time on the size and crystallinity of the products were investigated. The prepared samples were characterized using XRD, SEM, EDS and FT-IR techniques. The results showed that the synthesized ZSM-5 zeolite samples were almost pure and their crystallization was almost complete. The average particle size, as determined by Debye-Scherrer equation, was in the range of 20-42 nm. Increasing kaolin content on crystal size was more effective than increase in crystallization temperature and time. Additional evidences for the nano sized ZSM-5 zeolite were the asymmetric stretch vibration band at 1225 cm⁻¹ in the FT-IR spectra and TEM images. The scanning electron micrographs of the synthesized zeolites showed that they are spherical shape crystals.

Keywords: Nano zeolite, ZSM-5, Kaolin, Zeolite crystallization, Crystallinity

INTRODUCTION

ZSM-5, first prepared by Argauer and Landolt in 1971 [1], is a medium pore channel (~6 Å) zeolite with three-dimensional channels defined by 10 member rings. Due to its unique channel structure, thermal stability, acidity and shape-selective property, ZSM-5 has been used as sorbents and catalysts. It can be applied to petrochemical processing, fine chemical production, and liquid-gas separation [2,3]. Thus, increasing attention has been devoted to the synthesis, properties and applications of ZSM-5 zeolite.

Crystalline zeolites may be divided into three general classes based on their Si/Al ratio. Low-silica Zeolites are defined as having 1< Si/Al< 2, while intermediate Si/Al zeolites contain 2< Si/Al < 5 and high-silica zeolites with Si/Al > 5 were synthesized [4]. As the Si/Al ratio increases, the properties of the zeolite are significantly altered. The pathway of the crystallization process as well as the morphology and singular properties (crystal size and distribution) of the MFI-type zeolite are influenced by different variables, including the silicon and aluminum source [5], the template/silicon ratio, the nature of the cations present in the synthesis medium [5,6,7], the alkalinity [8,9,10,11], etc. Thus, it is well established that an increase in the SiO₂/Al₂O₃ and OH/SiO₂ molar ratios as well as a decrease in the H₂O/SiO₂ molar ratio in the initial synthesis solution leads to a decrease in the final particle size [12].

In this research we used kaolin as alumina source and investigated the effect of changing kaolin content, crystallization time and temperature on the size and...
crystallinity of the nano-sized ZSM-5.

EXPERIMENTAL

Materials and Procedure
The alumina source used was kaolin from Zonouze Co. Iran, the silica source used was silicic acid (Merck). The alkaline source was sodium hydroxide pellets (Merck), template source used was 40% solution of tetrapropylammonium hydroxide in water (TPAOH, Merck) and boric acid (Merck).

Nano sized zeolite was prepared according to a modified hydrothermal procedure which was reported previously by Miller for micro-sized ZSM-5 zeolite [13]. In this research kaolin was heated at 600 °C and a metastable phase referred to as metakaolin or dehydrated kaolin was obtained [14]. To synthesize the zeolite, 5 g of silicic acid was added to different amounts (1.0, 0.5 and 0.25 g) of metakaolin (70.05% SiO₂ and 18.44% Al₂O₃). Then 1.6 ml of TPAOH and 20 ml distilled water were mixed for one hour in a mixer. A solution of 0.42 g H₃BO₃ in 2.5 ml water was then added to the above mixture along with a NaOH solution (0.33 g in 2.5 ml water), and mixing continued for one more hour. The mixture was placed in a stainless steel reactor with internal Teflon vessel and heated at autogenous pressure at different crystallization temperatures and times. Finally, it was calcined in air at 500 °C for 8 h (yield 76%). The products were identified by XRD, FT-IR, TEM and SEM methods.

Characterization
X-ray diffraction (XRD) patterns were measured on a D 500 Siemens X-ray diffractometer using monochromatic Cu Kα radiation (30-40 kV and 40-50 mA), and the relative crystallinity of ZSM-5 was calculated based on the intensity of the peaks of 2θ = 22-25. The morphology and crystalline size of the samples were examined under a transmission electron microscope (TEM) Philips CM 200 FEG (Field Emission gun) and scanning electron microscope (SEM, LEO 440i) using samples coated with an Au film Elemental analysis was carried out using link, ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector.

The FT-IR spectra were recorded using Bruker Model Tensor 27 equipment. Calculation of degree of crystallinity was carried out using the IR data as follows: degree of %crystallinity = peak area at 542/peak area at 450 cm⁻¹ [15,16].

RESULTS AND DISCUSSION

X-Ray Diffraction
XRD pattern of synthesized zeolite is shown in Fig. 1. The peaks at 2θ = 7.96, 8.91, 14.00, 14.87, 20.92, 23.28, 23.97, 24.52, 26.66 confirmed ZSM-5 zeolite [17]. Figure 2a indicates XRD pattern of samples that crystallized by changing crystallization temperature from 120 °C to 180 °C. The crystallinity of as-synthesized sample, which was crystallized at 180 °C temperature, showed the highest

Fig. 1. XRD pattern of ZSM-5 types obtained from weight ratio of kaolin/silicic acid = 10 × 10⁻².