Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

High-temperature and short-time hydrothermal fabrication of nanostructured ZSM-5 catalyst with suitable pore geometry and strong intrinsic acidity used in methanol to light olefins conversion

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ARTICLE INFO

Article history:
Received 24 October 2017
Received in revised form 1 February 2018
Accepted 8 February 2018
Available online xxxx

Keywords:
ZSM-5
High temperature
Short time
Methanol
Light olefins
Deactivation

ABSTRACT

High temperature hydrothermal synthesis method was developed to preparation of nanostructured ZSM-5 molecular sieves at short crystallization time. A series of catalysts were synthesized at various temperatures and crystallization times for achievement of pure ZSM-5 phase with MFI structure. The synthesized catalysts were investigated with XRD, FESEM, EDX, BET-BJH, FTIR and TPD-NH_3 techniques. The results revealed that hydrothermal synthesis conditions generally affected the nucleation rate, particle size, textural properties and acidic nature of ZSM-5 catalysts. It was found that pure ZSM-5 materials with high crystallinity could be obtained at specific crystallization conditions of about 300 °C for 1.5 h and also 350 °C for 0.5 h. Increasing the hydrothermal temperature to 350 °C and decreasing the crystallization time to 0.5 h led to the formation of small particles with high specific surface area of 392 m^2/g. Furthermore, ammonia TPD spectra showed that ZSM-5(300-1.5) catalyst contained higher amount of acid sites and less acid strength compared to ZSM-5(350-0.5) catalyst. The catalytic performance of samples was studied for conversion of methanol to light olefins under different reaction conditions. Interestingly, the proper pore geometry along with the strong intrinsic acidity resulted in a tendency for excessive production of light olefins for ZSM-5(350-0.5) catalyst. The selectivity of light olefins over this catalyst was increased about 94% in the long time on stream (2100 min). Also, the possible reaction pathway for ZSM-5 synthesis at high temperatures was discussed in details.

1. Introduction

The two most important light olefins, ethylene and propylene, are key building blocks for the modern petrochemical industry [1–3]. The majority of olefins consumption is driven by the production of polymers (i.e. polyethylene and polypropylene) used for plastics, in addition to other important derivatives [4–6]. However, the demands for ethylene and propylene increase at different rates. The global propylene demand is forecasted to increase by 6–8% per year, which exceeds the forecasted growth in global ethylene demand of 4–6% per year [5,7]. The increased production of ethylene and the strong growth of propylene derivatives have driven up the price of propylene compared to ethylene [8–10]. Therefore, this situation results in an increasing gap between olefins demand and their production. On the other hand, the recent dramatic increase in oil prices is reviving a strong interest in the production of light olefins from non-petroleum source. The availability of low cost methanol along with the rise in propylene demand makes the methanol-to-olefins process viable [11,12]. The reaction mechanism for olefins production based on the first C—C bonds formation from C_1 entities occurred on the zeolite acid sites. A highly siliceous ZSM-5 based acid catalyst was primarily used in the MTO process to achieve the high selectivity to olefins [10,13,14]. ZSM-5 has the MFI structure with a three-dimensional pore system consisting of straight (5.6 × 5.3 Å) and sinusoidal channels (5.5 × 5.1 Å) [14,15]. The performance advantages of ZSM-5 material, resulting from the restrictive pore dimensions of MFI structure, are the low deactivation rate and enhanced stability attributed to its ability limited to growth of coke domains inside the channel system. The best method for synthesis of ZSM-5 is hydrothermal synthetic approach which is based on sol-gel chemistry under hydrothermal conditions [16–18]. The hydrothermal synthesis of molecular sieve

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https://doi.org/10.1016/j.apt.2018.02.009
0921-8831/

Please cite this article in press as: P. Sadeghpour, M. Haghighi, High-temperature and short-time hydrothermal fabrication of nanostructured ZSM-5 catalyst with suitable pore geometry and strong intrinsic acidity used in methanol to light olefins conversion, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.02.009

materials like ZSM-5 can be depended on the control of a large number of reaction variables (reactant, time, temperature, pressure, and so on) which are not independent of one another [10,19,20]. In addition to various hydrothermal synthesis strategies, several synthetic modification approaches have been invented as well. Among them, temperature and time of crystallization are two frequently adopted variables to tune the acidity and consequently the catalytic properties in terms of activity, selectivity and stability [21–23]. The synthesis temperature directly influences the crystallization and structure of the molecular sieve material formed during the hydrothermal synthesis [24–26]. As mentioned in the literature, the vast majority of ZSM-5 zeolites are hydrothermally prepared at low/moderate temperatures ranging from 120 to 250 °C [10,27]. The ZSM-5 molecular sieves which synthesized at low temperatures required a long synthesis time, usually several days, to form the crystalline materials [28,29]. In this regard, Barakov et al. [30] synthesized ZSM-5 catalysts via low temperature (100 and 170 °C) hydrothermal method for 3 days. They found that zeolite synthesized at 100 °C indicated the low amounts of acid sites and also broad distribution of acidic strength, in comparison with ZSM-5 prepared at 170 °C. The low temperature synthesis procedure, besides needing the high periods of time, can increase the energy consumption during the long crystallization time. To overcome these limitations, the high temperature hydrothermal synthesis method seems to be an effective idea to promote the synthesis route of ZSM-5 zeolites. High temperature synthesis is a valuable novel method for production of ZSM-5 catalysts with high purity of MFI phase in the short time. Although synthesis at high temperatures can produce pure phase at short time, as the synthesis time increases it is clear that the temperature not only affects the zeolitic structure formation but also what impurity phases are present [15,21,23]. Aghaei et al. [21] reported the presence of $AlPO_4$ impurity phase besides CHA structure of SAPO-34 which appeared by increasing the crystallization time at high temperature. They could reduce the formation of $AlPO_4$ phase by decreasing the synthesis time in constant temperature.

The much higher flux of heat which exerted to the synthesis gel at high temperature and short period of time can be the main reason for optimization of nucleation rate, crystal growth and uniform distribution of heat energy in the gel mixture [31,32]. As a result, the hydrothermal synthesis at high temperatures tends to form molecular sieve materials with a lower intercrystalline void space, uniform particle size, proper pore size distribution and high purity phase [23]. However, there are few publications which investigate the synthesis of zeolites at high temperature; there is no literature reported about the high temperature synthesis of ZSM-5 zeolite and its catalytic performance in the methanol to olefins reaction. Our research group was performed successful synthesis of pure ZSM-5 molecular sieve at high temperature for the first time. In this work, we studied the effects of high temperature (300–350 °C) and short time hydrothermal synthesis on physicochemical properties and catalytic performance of ZSM-5 catalyst. In this case, the short crystallization time was obtained at any temperature which resulted in the most pure ZSM-5 phase. The synthesized catalysts were characterized by XRD, FESEM, EDX, BET-BJH, FTIR and TPD-NH_3 analyses. The reaction pathway of ZSM-5 synthesis at high temperature was also investigated. In spite of the above mentioned objectives, it was important to achieve the pure MFI phase at short time which secured catalyst stability and enhanced the selectivity of light olefins. Therefore, the obtained catalysts were used in methanol to olefins process under different reaction conditions (temperature, space velocity, feed composition and time) and the effect of crystallization time and temperature on catalytic performance was studied in details.

2. Materials and methods

2.1. Materials

High temperature synthesis of ZSM-5 samples was carried out using sodium hydroxide (Merck, 97%), sodium aluminate (Riedel-deltane Haën, 99%), fumid silica (Aldrich, 99.8%) and tetrapropylammonium bromide (TPABr, 99.9%, Merck) as sources of Na, Al, Si and organic template, respectively. Ammonium nitrate solution (Merck, 99%) was also used for ion-exchange of Na^+ from the NaZSM-5 and replaced by NH_4^+. In addition, Deionized water (Kasra Company) was employed as reaction medium to prepare solutions.

2.2. Preparation and procedures

High temperature hydrothermal method was employed to prepare the ZSM-5 molecular sieve materials with tetra propylammonium bromide as the organic template. Fig. 1 shows the synthesis procedure for the preparation of ZSM-5 nanostructured catalysts via high temperature hydrothermal synthesis. In a typical synthesis, appropriate amount of NaOH was dissolved in deionized water, followed by the addition of sodium aluminate with vigorous stirring until homogenous solution was obtained. Tetra propylammonium bromide (TPABr) was added to the gel and stirred for 1 h before the addition of fumid silica as silicon source. The gel composition used throughout the synthesis procedures of the MFI-type materials was; $0.0025Al_2O_3$:$1SiO_2$:$0.1Na_2O$:0.1TPABr:$35H_2O$. After 24 h of stirring with a magnetic stirrer bar, the resulting gels were placed in a 90 mL stainless steel autoclave and heated at 300 and 350 °C for different crystallization times until a pure ZSM-5 phase was obtained. The products were washed with distilled water and dried at 110 °C for 12 h. Then, the prepared catalysts were calcined at 550 °C for 15 h to remove structure directing agent. In the next step, the Na^+ cations of NaZSM-5 were exchanged by NH_4^+ and refluxed two times with aqueous solution of 1.0 M ammonium nitrate for 12 h at 80 °C. The samples were dried at 110 °C for 12 h after each step of the ion-exchange process. Then, the HZSM-5 samples were calcined at 500 °C for 4 h in air ambient. The synthesized samples will be denoted as ZSM-5(x-y), where x stands for the crystallization temperature and y for the crystallization time.

2.3. Characterization techniques

The X-ray powder diffraction (XRD) data of the samples were collected by Bruker D8 Advance diffractometer using CuKα radiation in a scanning range of $2\theta = 5–55°$. The crystallinity of powder samples is measured based on the peaks intensity; generally the reflection peak at $2\theta = 23.2°$ of the ZSM-5(350-0.5) sample used as reference peak for calculation of the relative crystallinity. The line broadening of the peaks is also related to the crystallite size; the Scherrer equation leads to the measure of the crystallite sizes. Furthermore, a HITACHI S-4160 scanning electron microscopy (FESEM) was used to study the morphology and particle sizes of synthesized catalysts. The X-ray (EDX-dot mapping) analysis was performed to detect the chemical composition of the nanostructured catalysts using Scan MV 2300 Cam. The Brunner-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) were used for calculating the specific surface area and textural porosity of synthesized samples by Micrometrics ASAP 2020. Fourier-Transform infrared (FTIR) spectroscopy measurements were carried out to investigate the surface functional groups using UNICAM 4600 FTIR spectroscopy. The acidic strength and also amounts of acid sites on the surface of catalysts measured by ammonia-temperature

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