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Seed-assisted OSDA-free synthesis of ZSM-5 zeolite and its application in dehydrogenation of propane

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ABSTRACT

ZSM-5 is one of the most well-known members of zeolite family owing to its huge number of industrial applications due to its instinct acidity and well-defined micropore structure. It can be synthesized in a one or multi-step hydrothermal procedure employing versatile synthesis parameters. Here, seed-assisted OSDA (organic structure directing agent)-free synthesis method based on using TPABr-silicalite-1 as structure directing agent is proposed as an economical route considering reproducibility and short synthesis time benefits as well. This two-step synthesis technique exploits an enriched aluminum template-free precursor gel containing zeolite nuclei that attach and grow around high siliceous zeolite cores named as silicalite-1. The prepared ZSM-5 product was characterized using XRD, SEM, FT-IR, EDX, elemental mapping, ICP and N_2 adsorption–desorption techniques. Results confirmed the fully crystalline pure MFI structure of the obtained product. The catalytic behavior of the fabricated material as support was evaluated in the propane dehydrogenation reaction (PDH). The PtSn-based ZSM-5 catalyst maintained its activity to a certain level of about 31% propane conversion after 7 h time on stream with more than 89% total olefins selectivity. It seems that seeding along with using a cheap template like TPABr in the synthesis of seeds is an efficient method which has the potential to be emerged as a promising method for the ZSM-5 large-scale production.

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1. Introduction

It is more than six decades that lots of historical and hierarchical improvements have been evolved in materials sieving industry which were launched introducing aluminosilicate zeolites. Zeolites are three-dimensional porous mineral or synthetic crystalline materials with pore openings ranging from 0.2 to 30 nm which are commonly used as adsorbents and catalysts [1,2]. ZSM-5 as the most popular member of this family consist of SiO_4 and AlO_4 tetrahedra linking together forming pentasile chains that finally construct MFI structure with two different types of channels with dimensions around 5.5 Å. These pore openings besides its surface acidity give it size and shape sieving and catalytic properties which make it a great candidate for lots of chemical reactions like cracking, dewaxing, MTO, etc. [3–5]. ZSM-5 was firstly introduced by Argauer and Lendolt at mobile company in 1972 [6]. It can be effectively synthesized from the hydrothermal crystallization of an alkali aluminosilicate gel containing expensive template species as organic structure directing agents or space fillers.

There are two general OSDA-free synthesis protocols regarding ZSM-5 molecular sieve production namely template-free direct synthesis strategy in which an aluminosilicate gel is heated to form ZSM-5 crystals [7] and seed-assisted template-free method in which extraneous seeds are introduced to the aluminosilicalte gel to direct zeolite units toward the formation of MFI framework [8]. However, complexity in tuning the suitable Si-to-Al and Na-to-Si ratios, providing a precise control over synthesis parameters including types of raw materials, mixing, aging and crystallization conditions to obtain pure ZSM-5 phase, inhibiting any impurity formation such as mordenite zeolite, low product yield and low reproducibility restricted its evolution [9].

Synthesis of ZSM-5 applying high silica zeolite seeds (silicalite-1) as cores and an integrated enriched aluminum shell without using any extra template is a cost-effective route which has been under spotlight in last few years. Silicalite-1 is a microporous polymorph silica isostructural with the MFI structure consisting of eight five-membered oxygen rings. Although the role of seeds are not thoroughly comprehended but it is believed that silicalite-1 seeds with similar framework and common composite building units of ZSM-5 target zeolite are served as structure directing agent. In fact seeds provide a surface with TOH units on which formed zeolite units can attach, pile up and grow [10]. According to Cundy and Cox seeds

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behavior can be categorized in different ways [11]. Seeds can remain inert and solely act as pure cores on which zeolite units can deposit and grow or partially dissolve and lead to the secondary nucleation. It seems that seeds may act complicated and play role in more than one way. Therefore seed-assisted crystallization mechanism and intrinsic seed crystals and reactant gel interaction still require vast research. On the whole, this technique can address the environmental problems arising from the calcination of template and other volatile compounds which are not eco-friendly materials. In addition to, this technique combines several advantages including increasing the crystallization rate, shortening the crystallization time, boosting the solid yield, minimizing the template consumption, narrowing the crystal size distribution and suppressing the formation of undesired phases.

Effect of seeding step in ZSM-5 crystallization process was examined by introducing ZSM-5 crystals and pre-fabricated silicalite-1 nanoseeds into the original self-induction system [12]. Adoption of silicalite-1 nanoseeds had much more prominent effect which led to the formation of relatively small particles with promoted catalytic performance in benzene alkylation and xylene isomerization. Majano et al. [13] investigated the influence of diverse parameters like seed content and seed pretreatment in the synthesis of Na-ZSM-5 using seed-induced crystallization approach. Ren et al. [14] proposed a method based on seed surface crystallization method for the rapid and controllable synthesis of ZSM-5 zeolite with core–shell structure. Xue et al. reported the successful synthesis of NH_4-ZSM-5 zeolites with different Si/Al ratio and size by simply adjusting the amount of seeding suspension [15]. Addition of an organic additive and colloidal silicalite-1 seeds to the initial synthesis mixture for the fabrication of ZSM-5 were compared by Xu et al. [16]. More uniform fine crystals were obtained through growing of ZSM-5 shell around seeds that showed modified catalytic performance in MTG reaction with tuned product distribution.

So far seeding synthesis trend in the literature has been mostly around the usage of expensive templates such as tetrapropylammonium hydroxide (TPAOH) to achieve small uniform crystals but the yield of the assay has been lowered [17–20]. In this paper we produced ZSM-5 micro crystals through a seed surface crystallization method employing TPABr-silicalite-1 core crystals. Our aim is to propose an elaborate, efficient, facile and somehow cost-effective strategy for the synthesis of ZSM-5 zeolite regarding high solid product yield which would be applied for the large scale production. Besides, the performance of this material as catalytic support was evaluated in PDH reaction to convert propane to highly valuable propylene as one of the most important petrochemical building blocks with high selectivity and the performance of the prepared catalyst was compared with the literature.

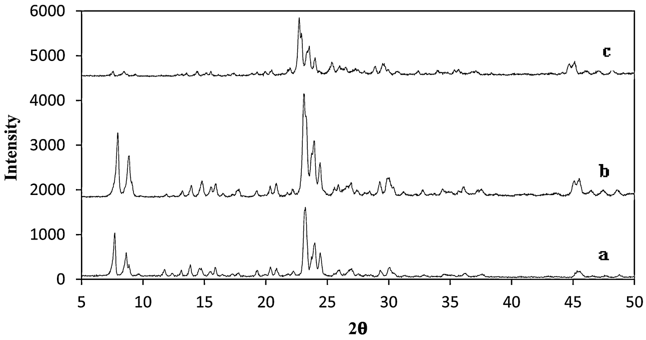

Fig. 1. XRD patterns of prepared samples: (a) silicalite-1, (b) Seed-ZSM-5 and (c) Ref-ZSM-5.

2. Experimental

2.1. Synthesis of zeolite

Silicalite-1 seeding suspension was prepared from the hydrolysis of silica sol (30%, Sigma) in the solution containing tetrapropylammonium bromide (99%, Merck) and sodium hydroxide (98%, Merck). After complete hydrolysis, the obtained mixture with molar composition of **1** SiO_2:0.2 TPABr:0.03 Na_2O:40 H_2O was hydrothermally treated at 150 °C for 24 h. For characterization, a portion of silicalite-1 product was isolated with centrifuging, washing with distilled water and drying. As the second step, a template-free gel was prepared by mixing sodium hydroxide, sodium aluminate (54%, Riedel de Haen) as aluminum source and same silica source to obtain a mixture with molar ratio of 60 SiO_2:1 Al_2O_3:4.2 Na_2O:1200 H_2O. The specified amount of silicalite-1 suspension with respect to 5% of total silica content was added to the mixture directly without any extra purification. Final crystallization step was performed at 170 °C for 24 h. The obtained product was recovered by centrifugation at 4000 rpm and repeatedly re-suspended in deionized water until the sol exhibited a pH value of about 9. Then it was dried and further calcined at 500 °C for 6 h with heating ramping rate of 1 °C/min.

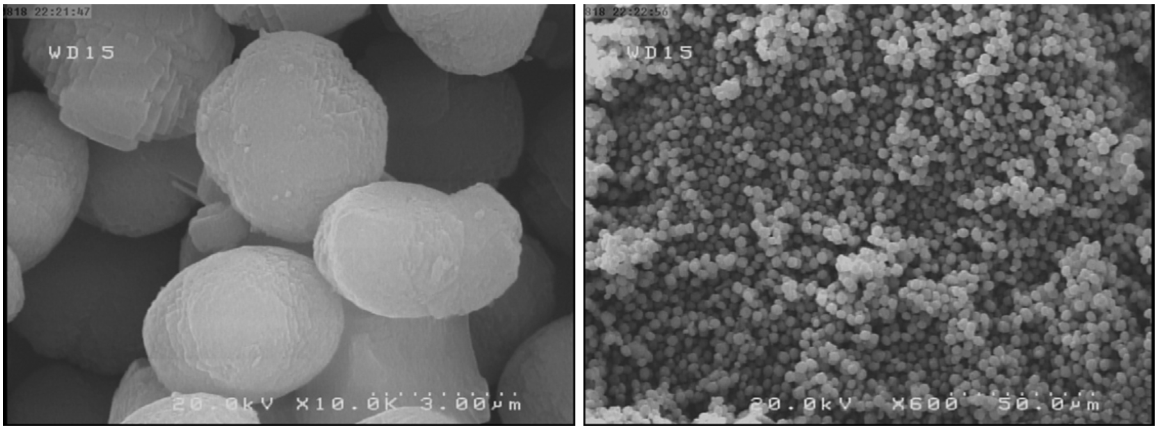

Fig. 2. FESEM micrographs of silicalite-1 sample.

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