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Synthesis and evaluation of seed-directed hierarchical ZSM-5 catalytic supports: Inductive influence of various seeds and aluminosilicate gels on the physicochemical properties and catalytic dehydrogenative behavior

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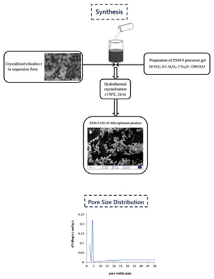
HIGHLIGHTS

- Synthesis of hierarchical ZSM-5 zeolites with different Si/Al molar ratios.
- TPAOH/TPABR-templated silicalite-1 seeding suspensions as structure directing agents.
- Presence of lamellar keatite assemblies at Si/Al $\geq$ 60 especially at TPAOH-silicalite-1-directed ZSM-5.
- Hybrid zeolites with supplementary meso/macro pores as catalytic supports in PDH reaction.
- Highest propene yield using PtSn/ZSM-5(Si/Al = 60) prepared from TABR-silicalite-1 seeds.

GRAPHICAL ABSTRACT



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ABSTRACT

TPABr-silicalite-1 and TPAOH-silicalite-1 seeding suspensions were employed as structure directing agents through a seed-directed synthesis strategy to prepare a series of organotemplate-free hierarchical ZSM-5 zeolites with three different Si/Al molar ratios of 30, 60 and 120. No secondary meso-generating agent was implemented to construct wide supplementary pores. The physicochemical properties of the products were characterized by XRD, FESEM, FT-IR, EDX, AAS, TGA and N_2 adsorption–desorption techniques. All zeolite samples with moderate hierarchy factors possessed a bi/tri-model porosity based on the governing nucleation mechanism and growth of zeolite crystals upon the surface of the silicalite-1 seeds. The prepared hybrid zeolites with intrinsic micropores and auxiliary meso/macro pores were served as the catalytic supports in propane dehydrogenation reaction to ascertain the influence of the seeding type, Si/Al ratio and consequent structural and particulate properties on the catalytic performance. The best catalytic result was acquired for Pt–Sn-based ZSM-5 catalyst, with Si/Al = 60, synthesized with less expensive TPABr-silicalite-1 seeds. Considerable activity (34.5% conversion) and high selectivity towards light olefins (90% for both ethylene and propylene); propylene in particular (84.5%) was observed after 4 h time on stream. This result is attributed to the high BET surface area and meso transport pores of the sample collaborated with high acidity to progressively impact on the reactivity and selectivity.

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1. Introduction

Zeolites are important industrial materials with broad range of applications as gas separator, ion-exchanger and more importantly catalyzer [1–3]. Socony Mobil#5 (ZSM-5) with MFI framework type has been regarded as the most popular member of zeolite family with well-defined channels system of molecular dimensions [4]. Its unique intricate porous structure and intrinsic surface acidity give it size and shape sieving and catalytic properties which are boon for lots of petrochemical reactions like cracking, aromatization, MTO and so forth [5–7]. ZSM-5 can be generally synthesized via the crystallization of an alkali precursor aluminosilicate hydrogel. The precursor hydrogel can be prepared following different protocols including organic template molecules as structure directing agents (SDA) and space fillers or excluding the usage of organic templates introducing extraneous seeds to induce the formation of ZSM-5 [8]. In fact in the latter method, seeds are provided to the aluminosilicalte gel to direct the zeolite units and drive the crystallization towards the formation of desired structure [9]. Cundy et al. [10] proposed different behaviors for gel-wrapped seeds wherein 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. Although seeds may act complicated and play role in more than one way, their essential role in supplying surface and exposing specific sites for the migration of TOH terminal units to attach and pile up in order to promote the crystallization process is evident. Short crystallization time, high crystallization rate, elimination of self-nucleation time-consuming step, low template consumption, high product yield and great control over crystal size distribution are the advantages accompanied by when using seed-directed environmentally benign synthesis method [11,12].

The importance of similarity of the building units between the seed and target zeolite, seed crystals surface area and recognition capacity of seeds TOH units on the crystallization behavior of template-free ZSM-5 have been studied by several groups [13,14]. Various seed-assisted synthesis systems were investigated by introducing seeds with different frameworks (FAU, MEL, and MFI) and pore structures. Framework similarity and existence of terminal TOH units proved to be the key factors for the nucleation process while large external surface area affected crystal size distribution significantly. Effect of seeding step on the kinetic of ZSM-5 crystallization process was examined sowing pre-fabricated ZSM-5 and silicalite-1 seeds into the original self-induction system [15]. Adoption of silicalite-1 nanoseeds had much more prominent effect which led to the formation of relatively small aggregates with promoted catalytic performance in benzene alkylation and xylene isomerization. Despite great endeavors have been dedicated to the investigation of the influence of synthesis parameters and underlying crystallization behavior in seeded systems, reports on the application of such materials are limited. A number of ZSM-5 zeolites prepared through seed-induced synthesis methodology using silicalite-1, ZSM-5 and NaY seeding suspensions were evaluated in the conversion of o-xylene [16], alkylation of naphthalene [17], fluid catalytic cracking [18], and hydration of cyclohexane [19] reactions and promising results were obtained. Well-preserved activity and high selectivity towards light olefins particularly propylene in FCC and o-xylene isomerization reactions suggests that this is an efficient economic approach for the production of ZSM-5 which will be a great benefit to industrial applications in selective production of light olefins in a controlled trend.

In recent years, the growth in propylene demand exceeded the growth in ethylene, opening up other technology opportunities focused primarily on propylene [20,21]. It is predicted that the demand for propylene derivatives will increase by 4% until 2020 and is expected to reach almost 100 million tons/yr in 2015 [22,23]. Generally, the worldwide propylene demand is mostly supplied from steam crackers and fluid catalytic cracking (FCC) units wherein propylene is produced as a byproduct [24]. However, the annual growing demand of propylene and the instability of crude oil price, the FCC unit's feedstock, cannot meet the gap between demand and productivity and consequent change of market [21,25]. Propane dehydrogenation (PDH) involves catalytic removal of hydrogen from propane to yield propylene which has received significant attention as an on-purpose alternative with high potential to cover the outgrowing propylene deficiency [26,27]. However, it suffers from equilibrium limitation and thermodynamical constraints due to strong endothermic character of the reaction disadvantageously. High reaction temperature is favorable, however it accelerates thermal cracking side reaction towards lighter hydrocarbons and coke which leads to low olefins selectivity and rapid deactivation. Therefore a great deal of work has been conducted to formulate catalysts exhibiting high catalytic properties and stability that can decelerate side reactions under severe conditions. Pt–Sn based ZSM-5 catalyst is a hydrothermally stable catalyst with good reactivity and shape selectivity because of its specific ten membered ring structure which can hinder the formation of bulky molecules and coke deposition [28,29].

It is well known that the application of a material is strictly correlated with its properties such as chemical composition, crystal size, morphology, network porosity, and acidity. In the light of this, we were encouraged to prepare ZSM-5 zeolites employing facile and low-cost seed-directed organotemplate-free synthesis strategy to ascertain the influence of textural and physicochemical properties of obtained materials on their catalytic performance in PDH reaction. Silicalite-1 high siliceous zeolite was selected as the directing seeds based on the presence of common building units between the parent seed and product zeolite and specific sites with enhanced recognition capacity. These sites attract formed aluminosilicate units in the gel to promote nucleation and subsequent crystal growth of target zeolite. Thus, several hierarchical zeolites with uniform crystal size distribution equipped with auxiliary mesopores have been fabricated by varying the Si/Al molar ratio and seeding suspension type namely, TPAOH and TPABr-templated silicalite-1. It is well proved that the Si/Al ratio is an important factor influencing physicochemical properties of zeolites, predominantly acidity. Several attempts have been made to clarify the influence of Si/Al ratio of ZSM-5-derived catalysts in various reactions including alkane dehydrogenations [30,31], MTBE production [32], craking of C_4 alkanes [33], and alkylation [34]. Therefore, the effect of Si/Al ratio on the catalytic features of prepared Pt–Sn based catalysts were assessed in PDH reaction aiming to produce light olefins in a controlled selective trend; highlighting propylene as the major product.

2. Experimental section

2.1. Materials

The chemical ingredients used in the syntheses were tetrapropylammonium bromide (TPABr, 99%), tetrapropylammonium hydroxide (TPAOH, 40%), nitric acid (HNO_3, wt. 65%), Platinum (IV) chloride ($PtCl_4$, 57.5% Pt), Tin (II) chloride ($SnCl_2$), and sodium hydroxide (NaOH pellets, 98%) which were purchased from Merck company. Colloidal silica (SiO_2, wt. 30%), was obtained from Aldrich and sodium aluminate ($NaAlO_2$, 54% Al_2O_3 and 41% Na_2O) was bought from Riedel-de-Haën company.