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Synthesis and application of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composite systems for propylene yield enhancement in propane dehydrogenation process

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ABSTRACT

Two types of zeolitic composite systems with binary hierarchical structures comprising ZSM-5 and SAPO-34 molecular sieves were synthesized employing different procedures. Obtained products were served as catalytic carriers for propane dehydrogenation reaction so as to promote the physicochemical properties of ZSM-5 support, enhance the propylene yield and reduce the formation of light compounds. ZSM-5/SAPO-34 was fabricated in a series hydrothermal procedure employing pre-heated ZSM-5 suspension followed by secondary growth of SAPO-34 layer whereas SAPO-34/ZSM-5 was synthesized using tetrapropylammonium bromide exchanged-SAPO-34 crystals and pre-reacted ZSM-5 slurry in a hydrothermal one-step process. The products were characterized by XRD, FESEM, EDS, FTIR, NH_3-TPD, and N_2 adsorption–desorption techniques to investigate the textural and structural properties of composite architectures. The catalytic performance of the bimetallic Pt-Sn-based composites were evaluated in propane dehydrogenation reaction and compared with those of physical mixture and single ZSM-5-derived catalysts. Either of composites represented improved catalytic performance due to the synergetic effect between ZSM-5 and SAPO-34, which promoted the catalytic properties of the samples. Catalytic reactivity of the composite catalysts was strongly dependent on the synthesis method and employed zeolite/zeotype ratio. Best result was acquired for Pt–Sn-based SAPO-34/ZSM-5 (Si/Al = 60) brand-new efficient composite with improved stability, boosted conversion and significant selectivity towards light olefins, propylene in particular.

1. Introduction

Zeolitic molecular sieves, with uniform three-dimensional nano-channels containing different portion and strength of acid sites are inevitable members of catalytic and separation processes [1–3]. It is well understood that both internal channels and external crystal surfaces with different acid strengths and shape sieving behaviors contribute in chemical reactions. Although external surface active sites are low in concentration, their role in catalytic reactions is not negligible bringing in mind the diffusional restrictions for reactants to reach active sites in the micropores [4]. Therefore, recent endeavors have been focused on the modification of external surface area of zeolites to enhance their reactivity and selectivity properties. The functionalization of the external surface of zeolites by different techniques such as acid leaching, steaming and element surface modification has been applied to induce mesopores and obtain a reasonable acid distribution [5–7]. However, partial destruction and species deposition may lead to a reduction in the effective diameter of pore openings and consequently fall the catalytic activity.

Another strategy for modifying the surface structure in order to manipulate the catalytic properties in a desired way is the growth of a continuous shell over core crystals. In this case, access to a core with specific properties is controlled by a shell which gives the composite high stability and functionality [8,9]. Bouizi et al. synthesized a series of microcomposites of different zeolite structure types including SOD-LTA (the first zeolite type represents the core and the second the shell material), BEA-LTA, FAU-MFI, MFI-BEA, BEA/MFI and MFI/MFI (silicalite-1/ZSM-5 and the reverse) [10,11]. The incompatibility between core material and shell precursor mixture in preparing several types of composites was circumvented successfully by the preliminary seeding of core crystals. However, the formation of core/shell structure in some cases like SOD/LTA remained a problem due to the compositional and crystallization fields incompatibilities between two structures.

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Therefore, the foremost importance of chemical compatibility and structural similarity of shell and core material, as well as the overlapping of crystallization conditions in producing an integrated shell around single crystals is an indispensable matter of fact [12,13]. Consequently, the successful synthesis of only few zeolitic compounds like MFI/MEL [14] composed of identical building units with different spatial arrangements, MFI/MFI [15,16] with similar building units and crystallization conditions, BEA/MFI [11] with entirely different structures and MOR/MFI [13,17] with a small overlapping between framework compositions and crystallization fields have been reported thus far. Above described samples exemplify the partial or complete overgrowth of a zeolitic material by another one normally taking place in a two-step synthesis methodology. There are two other important categories of composite materials, namely intergrowth as the result of intimate co-crystallization of zeolite materials with hybrid crystals and epitaxial growth phenomenon with specific selective orientation on a diversity of crystal faces which are usually obtained in a one-step synthesis technique. ERI/OFF [18], MFI/MEL [19], MAZ/MOR (ERC-1) [20], and BEA/MOR [21] are some frequent examples of intergrowth materials with similar planar building units. Besides, such a heteroepitaxial growth was reported by Wakihara et al. for a continuous chabazite film on a sodalite substrate with a patterned surface texture [22].

In spite of above described references, reports on the synthesis and application of aluminosilicate and silicoaluminophosphate binary structure composites are limited. Fan et al. [14] synthesized ZSM-5/SAPO-11 in a form of core/shell structure by means of in situ crystallization of SAPO-11 on ZSM-5 with modified dual porosity and acidity which showed good desulfurization activity and high liquid yield in hydro-upgrading FCC gasoline. Very recently, the preparation of a ZSM-5/SAPO-5 core/shell structure zeolite as FCC catalyst was reported applying a phosphorous precoating method [23]. Binary structure ZSM-5/SAPO-34 zeolitic composite has been fabricated and developed for MTO [24] and ethanol to propylene reactions [25]. In first case, series composite which was obtained through a consecutive hydrothermal crystallization procedure showed higher selectivity towards light olefins while in second one, physical mixture of individual ZSM-5 and SAPO-34 showed the highest propylene yield. Performed synthesis technique applying HZSM-5 powder and SAPO-34 precursor gel in a one-step hydrothermal crystallization was not successful in producing a composite with improved performance.

As far as we are concerned, no specific bi-phase composite structure has been recommended for propane dehydrogenation (PDH) reaction for the selective production of light olefins in a controlled trend; highlighting propylene as the major product. In recent years, the growth in propylene demand exceeded the growth in ethylene, opening up other technology opportunities focused primarily on propylene. Generally, the worldwide demand for propylene is well supplied from steam crackers and FCC units providing propylene as a byproduct [26]. However, the annual growing demand of propylene cannot meet the significant change of market, bringing in mind the instability of crude oil price as well. PDH involves catalytic removal of hydrogen from propane to yield propylene which has been proposed as a great on-purpose alternative with high potential for covering the major propylene deficiency [27,28]. But it suffers from equilibrium limitation and thermodynamical constraints. It is crucial to formulate a catalyst exhibiting high catalytic properties and stability that can decelerate side reactions under severe conditions. Pt–Sn-based zeolite Socony Mobil#5 (ZSM-5) catalyst is a hydrothermally stable catalyst with good reactivity but low propylene yield since the present strong acid sites in its structure transform propylene to heavy bulky products [29–31]. It seems that contribution of a system with high quality sieving network like SAPO-34 can alleviate the aforementioned problem and increase propylene yield [32,33].

In this contribution, synthesis of ZSM-5/SAPO-34 binary nanostructured composite by means of a sequential crystallization method is reported. Additionally, an efficient convenient pathway is proposed to preserve SAPO-34 crystals in the strong basic precursor media of ZSM-5 to produce a novel bi-phase SAPO-34/ZSM-5 zeolite composite. Despite SAPO-34 and ZSM-5 zeolites have neither similar framework compositions nor chemical compatibilities, pre-treatment step accomplished to boost up SAPO-34 robustness in the synthesis media. Combination of useful physicochemical properties of these two types of zeolites with structural codes of CHA and MFI into a hierarchical composite can improve surface properties and lead to a modified distribution of active centers. In this way a great organization of catalytic, sieving and adsorptive functions of both flanking structures is combined that can increase the application area of these materials. The influence of properties on the catalytic performance of Pt–Sn-based composite catalysts are compared with those of single ZSM-5 and physical mixture of individual ZSM-5 and SAPO-34 in the PDH chemical reaction to convert propane to highly valuable propylene as one of the most important petrochemical building blocks.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), aluminum isopropoxide (AlP, 98%), polyethylene glycol (PEG, MW = 4000), tetraethylammonium hydroxide (TEAOH), wt. 20%), tetrapropylammonium bromide (TPABr, 99%), diethylamine (DEA, wt. 99%), ortho-phosphoric acid (H_3PO_4, wt. 85%), hydrochloric acid fuming (HCl, wt. 37%), nitric acid (HNO_3, wt. 65%), Platinum(IV) chloride ($PtCl_4$, 57.5% Pt), Tin(II) chloride ($SnCl_2$), 2-propanol (C_3H_8O) and sodium hydroxide (NaOH pellets, 98%) were purchased from Merck company. Colloidal silica (SiO_2, wt. 30%), tetraethylammonium hydroxide (TEAOH, wt. 35%) were obtained from Aldrich. Sodium aluminate ($NaAlO_2$, 54% Al_2O_3 and 41% Na_2O) was bought from Riedel-de-Haën company. Commercial Pt–Sn–K/γAl_2O_3 catalyst (Pt = 0.6 wt.%, Sn = 0.8 wt.%, K = 0.8 wt.%, surface area = 200 m^2/g, total pore volume = 0.65 cm^3/g) in form of spheres was supplied by Procatalyse company.

2.2. Synthesis procedures

2.2.1. Preparation of ZSM-5/SAPO-34 composite zeolite

In this section two series of composites referred as ZS1 and ZS2 were greatly synthesized. In the first case, ZSM-5/SAPO-34 binary composite synthesis was carried out following a sequential crystallization. Firstly, ZSM-5 core crystals were synthesized according to the seeding method applying silicalite-1 seeds as SDA (structure directing agent). A template-free aluminosilicate precursor gel was prepared by the hydrolysis of sodium aluminate and colloidal silica as Si and Al sources with the molar composition of 60 SiO_2:1 Al_2O_3:4.2 Na_2O:1200 H2O. Sodium hydroxide was employed as the alkali agent to attain the suitable PH of synthesis media (PH ~12) and thereafter a certain amount of silicalite-1 (equal to 5% of total silica amount) was added to the reaction mixture. The homogenous gel was moved to a 150 ml stainless steel autoclave and heated at 170 °C for 24 h to crystallize. In the second step, SAPO-34 precursor gel with molar ratio 1 Al_2O_3:0.5 SiO_2:0.8 P_2O_5:0.1 HCl:1.8 DEA:0.2 TEAOH:0.05 PEG:60 H_2O was obtained using TEOS, AlP and H_3PO_4 as Si, Al and P sources, respectively. TEAOH and DEA mixture was employed as structure directing agent and PEG