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Synergy effect between hierarchical structured and Sn-modified H[Sn, Al]ZSM-5 zeolites on the catalysts for glycerol aromatization

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ABSTRACT

Hierarchical H[Sn, Al]ZSM-5 zeolites were successfully prepared by hydrothermal method with directly incorporating Sn species into framework of HZSM-5 zeolites followed by alkali treatment. The prepared samples were characterized by XRD, BET, SEM-EDX, TEM, NH_3-TPD, FT-IR and Py-IR. The results indicate that Sn species were successfully incorporated into HZSM-5 zeolites. The catalytic performances of all prepared zeolites were evaluated by glycerol aromatization. The highest catalytic performance of GTA synthesis was observed with H[Sn, Al]ZSM-5 treated with 0.3 M NaOH (32.1% carbon yield of BTX aromatics and 13 h catalyst lifetime), which was prior to the pure HZSM-5 (17.8% carbon yield of BTX aromatics and 3 h catalyst lifetime). The remarkably improved performance in catalytic activity and stability of H[Sn, Al]ZSM-5/0.3AT zeolitize could be attributed to synergy effect between Sn species doped into HZSM-5 zeolite and the generated micro-mesoporous structure by alkali treatment.

1. Introduction

Benzene, toluene and xylene (BTX), as the important raw materials in the organic chemical industry, are widely used in in the medicines, perfume and dyestuff. Traditionally, the commercial processes for almost BTX production mainly relied on petrochemical technologies such as reforming, cracking and pyrolysis using non-renewable petroleum which may be dried up in the following 40 years at the current consumption [1]. Therefore, with the exhaustion of petroleum resources, it is imperative to seek an effective route for BTX synthesis to replace processes using crude oil. At present, the route for BTX production derived from glycerol is attracting researcher's interests and is regarded to be remarkably promising. As we all know, glycerol, as the major by-product of fossil fuels, is formed during the process of biodiesel production and became a glut of glycerol chemical market in recent years with the tremendous growth in the worldwide biodiesel market [2–4]. Unfortunately, the separation and purification of the raw glycerol need consume a lot of energy and cost. As a result, most of the by-products was directly discarded, which causes the serious environment pollution and energy waste. Based on these perspectives, multiple catalytic process of glycerol to high-value chemicals, such as 1, 2-propanediols [5], 1, 3-propanediol [6], polyhydroxyurethanes [7] and polyglycerols [8] have been investigated. Similarly, transformation of glycerol to aromatics not only could provide a new pathway to produce aromatics and consequently meet the increasing market demand of BTX, but also can promote the sustainable development of associated biomass energy.

ZSM-5 zeolites were comprehensively used as catalysts during the alkylation reaction, isomerization reaction and aromatization reaction because of their high surface areas, unique three-dimensional pore channel structures and adjustable acidic sites. In recent years, the successful researches concerning methanol to aromatics (MTA) over ZSM-5 zeolite catalysts were extensive, indicating distinguished properties of the zeolite [9,10]. Similarly, during the GTA process, HZSM-5 zeolite exhibits superior catalytic performance due to its unique acid properties and shape-selectivity [11]. However, a fly in the ointment was that single HZSM-5 zeolites during the GTA process has outstanding performance of poor catalytic activity and stability [12]. Generally, some modification to ZSM-5 is required to be done to improve catalytic activity and stability in GTA reaction by introducing some metal species such as, Cu [13], Ag [14], Fe [15], Zn [16] and Sn [17]. As reported, Ag/ZSM-5

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zeolite emerges splendid activity at initial reaction, but deactivated very soon. Compared to other metal species, Sn is most attractive owing to its low cost and high effectiveness for glycerol aromatization [17]. The BTX yield can reach to 21.1 wt% over Sn-modified HZSM-5 [17], but the catalyst stability did not reach the acceptable level [18]. Because, metal-modified HZSM-5 was prepared by impregnation method, the metal species is always either remaining on the outer catalytic surface [19] or blocking in the micropore channels, which could enhance the diffusion resistance of reactants and products and further prevent feedstocks from contacting the active sites [20,21]. At present, several reports indicate that the catalytic properties of HZSM-5 zeolites by direct incorporation of heteroatom into framework are more effective and stable than the traditional impregnation of metal species on HZSM-5 during the aromatization process in both catalyst lifetime and selectivity of BTX. For instance, Miao et al. [22] reported that the incorporation of Fe species could enhance the activity and stability of monocrystalline H[Fe, Al]ZSM-5 catalysts synthesized by hydrothermal method in methanol to gasoline (MTG) process. Sun et al. [18] found that the preparation of nano-sized H[Zn, Al]ZSM-5 zeolite presented high BTX yields and stable aromatization performance over MTA reaction due to the well dispersion of Zn species in the zeolite. Gabelica et al. [23] surveyed that incorporation of Sn into zeolite framework was an excellent approach to improve catalytic efficiency and activity, however, the acid properties and catalytic performance were not investigated.

Although the presence of unique microporous in zeolite is a favor for the improvement selectivity to BTX, while the sole micropores impose significantly diffusion limitation of products that results in hampering the activity and stability of catalysts along with time, especially when the reaction is significantly faster than diffusion in the micropores [24]. Thus, a lot of research on the optimization of ZSM-5 zeolites by alteration of preparation methods or modification technologies has been devoted to solving both the activity and stability of catalysts problems. Among several promising strategies of introducing considerable intra-mesopores into zeolite or shorting the pathway of pore channel (e.g. syntheses of nanosized [22,25], post-synthesized mesoporous [26] and ordered mesoporous materials [27]), which can decrease the contact time of reaction intermediates, the post-synthesis treatment has been proved the simplest and the most effective method. For example, Bjorgen et al. [28] found that catalytic lifetime and selectivity to BTX was significantly improved towards the desired gasoline fraction when MTA process was carried out on the hierarchical HZSM-5 treated by alkali solution. Mochizuki et al. [29] investigated the catalytic performance in hexane cracking over HZSM-5 treated by desilication and discovered that the alkali-treated was more stable against coke deposition due to the larger number of pore entrance.

Taking into account these attractive results, the H[Sn, Al]ZSM-5 with incorporation of Sn species by hydrothermal synthesis were prepared. Furthermore, the hierarchical H[Sn, Al]ZSM-5 after alkali treatment were tested in GTA process to investigate the synergistic effect between active species and hierarchical pores. The catalysts were characterized and the correlate of catalyst properties and catalytic performance in GTA reaction was also discussed in detail.

2. Experimental

2.1. Catalyst preparation

The HZSM-5 and H[Sn, Al]ZSM-5 were synthesized using tetraethyl orthosilicate (TEOS, 28.4 wt% SiO_2, Sinopharm, China) and sodium aluminate ($NaAlO_2$, 41 wt% Al_2O_3, Sinopharm, China) as Si and Al sources, respectively. Tetrapropylammonium hydroxide (TPAOH, 25 wt% aqueous solution, Ourchem, China) was used as structure-direction agent (SDA). Other chemicals, such as sodium hydroxide (NaOH, AR, Sinopharm, China), ammonium chloride (NH_4Cl, AR, Sinopharm, China) and tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, AR, Sinopharm, China) were directly used in the as-received form.

The catalysts were synthesized by a typical hydrothermal synthesis method. The gel mixtures with the chemical compositions of Al_2O_3: SiO_2: TPAOH: M: H_2O = 1: 200: 45: 0.35: 4000 (M stands for Sn) were generated just as follows: A calculated amount of $NaAlO_2$ and TEOS was successively introduced into the TPAOH aqueous solution under continuously stirring at 313 K for 5 h. A $[Sn(NH_3)_4]^{4+}$ aqueous solution, prepared by the reaction of ammonia with $SnCl_4$, was dropwise added into the above-mentioned mixtures under vigorous stirring at 313 K. Then the pH of the resulting gel was adjusted to 10 with the addition of ammonia solution. The gained gel mixtures were stirred at 313 K overnight and then transferred into a Teflon-lined autoclave for hydrothermal synthesis at 443 K for 5 d in an oven. The zeolite was separated by centrifugation, and washed several times with deionized water until the pH value near 7. Finally, after dried at 353 K overnight, the precipitate was calcinated at 823 K for 5 h.

Hierarchical NaZSM-5 and Na[Sn, Al]ZSM-5 was separately prepared by mixing 10 g of as-synthesized NaZSM-5 and Na[Sn, Al]ZSM-5 and 200 g of 0.3 M NaOH solution at 343 K. After being stirred for 2 h, resultant solids were collected by centrifuging, washing and drying. Finally, HZSM-5/0.3AT and H[Sn, Al]ZSM-5/0.3AT were obtained by ion exchange with 1 mol/L NH_4Cl under solid to liquid ration of 1:20, and the ion-exchange process was repeated two times followed by calcination at 823 K for 4.5 h after dried at 353 K for 12 h.

2.2. Characterization of catalysts

Powder-X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a BRUKER D8 Focus diffractometer using Cu Kα radiation ($\lambda = 1.54506$ A) with $10^\circ \cdot min^{-1}$ in the 2θ range of 5-60°. The surface areas and pore volumes were determined by using a Beishide 3H-2000 instrument. Prior to the measurement, the zeolites were degassed under vacuum at 473 K for 12 h. The specific areas were calculated by using the Brunauer-Emmett-Teller (BET) method. The t-plot method was employed to evaluate both the micropore area and volumes. The mesopores volumes were calculated by the BJH method and the total pore volumes were derived from the t-plot method. Field emission scanning electron microscopy (FE-SEM) on FEI Inspect F50 was used to determine both the size and morphology of zeolite particles, additional the energy spectrum of EDX (energy dispersive X-ray spectrometer) to measure the element, with quanta 250. Prior to the measurement, the samples were prepared on a carbon pad and sputtered with gold to obtain the necessary conductivity. Transmission electron microscopy (TEM) using JEM-2100 was used to determine the lattice fringe and crystal axial direction of the zeolite particles. Fourier-transform infrared (FT-IR) was used to record the diffuse reflectance infrared spectra of the samples. Prior to the measurement, the samples were dispersed in KBr at a weight ratio of 1:100 and then pressed into thin wafers with a diameter of 13 nm. Temperature programmed desorption of ammonia (NH_3-TPD) was carried out to measure the acidity of the samples on an automated adsorption instrument (TP-5076). 100 mg samples were initially preheated at 400 °C for 1 h with helium atmosphere and then cooled down to 100 °C and further exposed to NH_3 for half an hour. Subsequently, after purifying with helium (30 ml/min) at least 50 min, the weakly and physically absorbed NH_3 on the sample was removed, and at last, the samples were heated up to 600 °C at a