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Size effect of TS-1 supports on the catalytic performance of PtSn/TS-1 catalysts for propane dehydrogenation

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ABSTRACT

Supported noble metal catalysts are extensively used for propane dehydrogenation in both the academy and industry. When the active components are fixed, the variation and improvement of the support will significantly affect the performance of the catalyst. Here we first prepared a series of PtSn/TS-1 catalysts with systematically controllable sizes of TS-1 zeolite supports. The particle sizes of the as-prepared TS-1 zeolite supports are from 100 nm to 5.72 μm. The TS-1 supports exhibited only weak acid sites, which avoids some side-reactions such as cracking and coking. The minimal size TS-1 (~100 nm)-supported PtSn catalyst gave the best catalytic performance and almost preserved the activity after a four-cycle reaction. The improved activity is ascribed to the hierarchically porous structure of the small-sized TS-1 sample, whereby diffusion hinders the mass transportation no more as certified by the Weisz–Prater criterion. The relationship between propane conversion and support size was fitted by a quadratic function. To further investigate the deactivation process, the species of deposited carbon was analyzed by in situ Raman methods. The work gave a new strategy for improving the catalytic performance of conventional supported catalysts in the PDH reaction, as well as some other heterogeneous catalysis.

1. Introduction

In recent decades, ample shale gas reserves are continuously being explored the world over, which provides a stable and cheap source for the efficient utilization of alkanes, including propane. Propylene is among the most important basic petrochemical materials due to its plentiful downstream products. Consequently, dehydrogenation of propane, as a new way to increase the production of propylene, has attracted steadily rising interest in the chemical industry.

Platinum- or chromium oxide-based catalysts are most widely used in commercial propane dehydrogenation (PDH) processes [1]. As an environmentally friendly material, the former achieves much wider application. After introduction of tin oxide, PtSn-based catalysts exhibit higher catalytic activity and better tolerance of coke formation [2]. To further increasing the production of propylene, a great deal of effort has been devoted to improving the catalytic performance of PtSn-based catalysts. The mechanism for the activation of C—H bonds in propane has been investigated in detail [3,4].

Because the dehydrogenation of C_3H_8 is endothermic and requires a high temperature (about 863 K), deep dehydrogenation also happens with the by-product of deposited coke; the lifetime of commercial Al_2O_3-supported catalysts is too short to resist deactivation under reaction conditions [5,6]. In comparison, with intrinsic pores of molecular size, zeolites have been widely used in the petrochemical industry as supports or solid-acid catalysts [7–9]. It has been demonstrated that zeolites are composed of SiO_4- or AlO_4- tetrahedra, and their ordered multi-membered ring channel system is regarded as inhibiting the formation of carbon species [10,11]. However, the channels of microporous aluminosilicates are surrounded by catalytically active strong acid sites, which cause the cracking of alkanes and cut back the desired products [12]. To address this problem, methods are still needed to reduce the acid content and strength by adding alkali (earth) metal. The application of new zeolites with lower acidity is still promising and important to the main reaction.

In addition, the kinetic diameter of propane is 0.47 nm, which is smaller than but very close to the pore diameter of ZSM5 zeolite (0.51 × 0.56 nm) [13,14]. Their internal pores make the transfer

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of propane or propylene difficult, and the drawback of diffusion also causes partial poor distribution of the product, which further hinders the improvement of catalytic performance. Fortunately, recent progress in zeolites points to a new strategy for overcoming this restriction by integrating micro- and mesopores [15–17]. A hierarchical porous molecular sieve can be prepared by controlling the morphology of zeolites with ultrathin slices or direct creation of a secondary pore system. Al-containing zeolites usually lead to further side reactions such as coking of isomerization, whereas TiO_x ($x < 2$) species are believed to accelerate the selectivity of propylene and stability of the catalyst [18]. Electrons can transfer from TiO_x species to Pt atoms, and thus electron-rich Pt particles tend to inhibit the adsorption of propylene and improve the selectivity to propylene

As is known, the catalytic performance is significantly affected by the electronic interactions between metal and support in heterogeneous catalysis [19–22]. For the traditional PtSn-based catalysts, improvement in the type or morphology of the support is a promising method for achieving better catalytic performance.

In the present work, a series of TS-1 zeolites were hydrothermally synthesized with methodically controllable crystal sizes and then used for the first time as supports for PtSn in the reaction.

Importantly, this strategy allows supports with similar micropore systems but different crystal sizes to be targeted for better catalytic performance. The catalysts were characterized by means of SEM, XRD, BET, UV-DRS, Raman, TEM, and XPS. Their microscopic structures are similar, such as the coordination state of titanium, the area of micropores, and acidity. The external surface area of as-prepared TS-1 zeolite increases with the reduction of crystal size, because a secondary mesopore system is gradually formed among the small crystal particles. The hierarchical pore system is beneficial for mass transfer and provides extra interfacial area for the contact of active components and reactants. Moreover, the TS-1 sample has a three-dimensional channel system similar to that of ZSM5 MFI zeolite but exhibits only weak acid sites, which avoids some side reactions such as cracking and coking. Supports with suitable physical morphology (small crystal size accompanied by hierarchical pore) and chemical properties (acidity) are of fundamental importance for the PDH reaction.

2. Experimental

2.1. Catalyst preparation

All TS-1 zeolites were synthesized according to the traditional hydrothermal method with a permanent Si/Ti molar ratio of 50 [23–25]. By changing the molar ratio of tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), and water in the sol system, the crystal size of TS-1 could be adjusted. Moreover, addition of isopropanol and variation of synthesis temperature also led to different crystal sizes. In a typical synthesis, 10 g of TEOS together with tetrabutyl titanate (TBOT) was dissolved in an aqueous solution of TPAOH (14.6 g, 20 wt.%). The mixture was stirred in ice water for 1 h and heated to 70 °C for 3 h. Then 12 g of isopropanol (IPA) was added and stirred for 1 h. The molar composition of the final gel was 1 SiO_2:0.02 TiO_2:4 IPA:0.3 TPAOH:35 H_2O. The solution was subjected to a hydrothermal crystallization process at 170 °C for 4 days. After repeated washing and drying, the precursors were calcined in air at 550 °C to get TS-1 zeolites of 100 nm. The absence of isopropanol in the gel leads to the growth of TS-1 zeolites from 100 to 200 nm and the size of the zeolite can further increase to 300 nm when the amount of TPAOH is reduced by 20%. When the mixture with a molar composition of 1 SiO_2:0.02 TiO_2:0.6 TPAOH:35 H_2O was directly stirred at 60 °C for 5 h, the final size of the TS-1 zeolite is 1 μm. The addition of isopropanol (1 SiO_2:4 IPA) results in smaller TS-1 zeolites (500 nm) and the substitution of TEOS for silica sol assists in obtaining the largest TS-1 crystals of 5.72 μm. The nominal chemical compositions of the starting materials for the synthesis of TS-1 is given in Table S1 in the Supplementary Material.

Bimetallic PtSn/TS-1 catalysts were prepared by the incipient-wetness impregnation method. A water solution of $H_2PtCl_6{\cdot}6H_2O$ and $SnCl_4{\cdot}5H_2O$ with the molar ratio 1:2 was added dropwise to the prepared TS-1 zeolites. After constant stirring, the mixture was treated by ultrasonic vibration and dried at 50 °C for 48 h. Finally, the mixture was roasted at 773 K for 4 h to get ae series of PtSn/TS-1 catalysts with different support sizes. The contents of platinum and tin in the final catalyst were fixed at 0.5 and 0.6 wt.%, respectively.

2.2. Characterization

Scanning electron microscope (SEM) images were obtained on a SU8010 apparatus operating at 5 kV. The samples were coated with gold before the SEM measurements. The X-ray diffraction patterns of PtSn/TS-1(x) catalysts were obtained on a Shimadzu X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA). The scanning range 2θ was 5° to 50° with a rate of 5°/min. The textural properties of PtSn/TS-1 catalysts were determined on an automatic N_2 adsorption–desorption instrument (Tristar II 2020). Before measurement, the catalysts were degassed under vacuum at 350 °C for 4 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas of the samples and the Barrett–Joyner–Halenda (BJH) model was employed to calculate the pore size distribution in the desorption branches of the isotherms. Diffuse reflectance UV–vis spectra of the catalysts were recorded using a Hitachi U-4100 spectrometer at 200–800 nm. The (in situ) Raman spectra of the catalysts were recorded on a Renishaw inVia Reflex Raman spectrometer. The laser line at 532 nm was used as the exciting source with a maximum of 1 mW at the surface of the sample. Temperature-programmed desorption of ammonia (NH_3 TPD) measurements were performed to analyze the acidity of catalysts. A thermal conductivity detector (TCD) was used to record the TPD profiles from 100 to 600 °C at a heating rate of 10 °C/min. Transmission electron microscopy (TEM) measurements of the catalysts were carried out on a JEOL JEM-2100 electron microscope equipped with a field emission source working at 200 kV. The X-ray photoelectron spectra (XPS) were obtained with a PerkinElmer PHI-1600 ESCA spectrometer using Mg*K*α radiation ($h\gamma = 1253.6$ eV). The values of binding energies were calibrated with the C1*s* peak of contaminant carbon at 284.6 eV.

2.3. Catalytic activity tests

The catalytic performance of PtSn/TS-1 catalysts for propane dehydrogenation was tested in a quartz tubular microreactor with a fixed bed. Before evaluation, the catalyst was prereduced in H_2 at 773 K for 4 h. The reaction was carried out under the conditions following: reaction temperature 863 K, atmospheric pressure, feed gas including C_3H_8, H_2, and N_2, molar ratio of C_3H_8:H_2:N_2 1:1:4, WHSV 3 h^{-1}. A SP-2100 gas chromatograph was employed to analyze all reaction products. Gas phase products were separated on an aluminum capillary column and their concentrations were detected by an H-ionization flame detector. The propane conversion was determined from the inlet and outlet propane mole fractions as

$$C(C_3H_8) = \frac{n^{\text{inlet}}_{C_3H_8} - n^{\text{outlet}}_{C_3H_8}}{n^{\text{inlet}}_{C_3H_8}} \tag{1}$$