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Article

Ordered mesoporous Sn-SBA-15 as support for Pt catalyst with enhanced performance in propane dehydrogenation

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ABSTRACT

A series of Sn-incorporated SBA-15 materials with high specific surface areas and highly ordered mesoporous structures were synthesized by a facile one-pot method and used as catalyst supports. A reference sample was also prepared using a conventional impregnation method. The catalysts were characterized using various methods, and their activities in propane dehydrogenation were investigated. The incorporation of Sn into the SBA-15 matrix led to strong interactions between Sn species and the support, and these helped to maintain the oxidation states of Sn species during the reaction. Substitution with Sn changed the interfacial properties of the Pt species and improved the function and effect of the Sn promoter. The catalytic activities and stabilities of the Pt catalysts supported on Sn-incorporated SBA-15 were better than those of the impregnated sample. However, the catalytic performance deteriorated when an excessive amount of Sn was introduced and the interactions among Pt, Sn species, and the support became weaker. The Pt/0.5Sn-SBA-15 catalyst gave the best propene selectivity, i.e., 98.5%, with a corresponding propane conversion of about 43.8%.

1. Introduction

Propane is an important raw material in the production of various chemicals and of great practical value in various reactions such as polypropylene, propylene oxide, and acrylonitrile syntheses. Steam cracking and fluidized catalytic cracking of naphtha are common processes for the commercial synthesis of propene [1–3]. Recently, propane dehydrogenation has been widely investigated as an effective approach to propene production because of the continuing decrease in fossil oil resources and the increasing market for propene [4–6]. Low-cost saturated hydrocarbons can be converted to value-added olefins by propane dehydrogenation, and this route is economically competitive [7]. Propane dehydrogenation is a highly endothermic and equilibrium-limited reaction, therefore a high temperature is needed to obtain a satisfactory yield of propene [8]. However, problems such as hydrocarbon cracking and coke formation arise with increasing reaction temperature, and these lead to decreases in the activity and stability of the catalyst [9].

Currently, catalysts based on chromium oxide or Pt are the main catalysts being investigated for propane dehydrogenation. Cr-based catalysts have been extensively researched, but their practical applications are limited because of severe pollu-

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tion by chromium [10,11]. Pt-based catalysts show good initial activities in propane dehydrogenation; this is because Pt activates C–H bonds without promoting C–C cleavage [12,13]. However, undesired thermal cracking and coke deposition rapidly deactivate these catalysts [14]. The development of efficient catalysts with high selectivities for propene and excellent anti-coking abilities is therefore important.

Considerable research has been devoted to developing methods such as promoter addition for improving the catalytic performances of Pt-based catalysts for propane dehydrogenation. The introduction of Sn promoters into a Pt-based catalytic system effectively improves the catalytic activity, resistance to coke formation, and operating lifetime of the catalyst [13,14]. The Sn promoter modifies the properties of Pt-based catalysts via geometric and electronic effects [15,16]. A number of studies have shown that the presence of Sn reduces the Pt particle size and also alters the electronic environment of Pt as a result of migration of positive charges from Sn^{n+} or Pt-Sn alloys [17,18]. It has been proposed that an oxidized Sn promoter can greatly improve the catalytic performance, but metallic Sn acts as a poison [19]. The preparation method, support properties, and metal loading clearly affect the performances of Pt-Sn catalysts [20]. Supports with large surface areas and well-distributed pore sizes to improve dispersion of the metal particles are preferable [21]. The use of SBA-15 as a support for Pt-Sn catalysts for propane dehydrogenation may therefore be an excellent choice . The mesoporous structure of SBA-15 enables it to confine and stabilize Pt nanoparticles and prevent particle agglomeration, making it a good host [22].

The reported methods for introduction of a Sn promoter almost all involve traditional post-synthesis procedures [23,24]. Such processes often give uneven distributions of Sn species, and block the pores and channels, leading to a decrease in the surface area and loss of efficiency of the Sn promoter [25]. This paper describes the preparation of homogeneous Sn-SBA-15 composites using a facile one-pot hydrothermal method. In contrast to traditional methods, the direct synthesis of Sn-SBA-15 can prevent pore clogging and achieve a good distribution of Sn species in the silica matrix. Sn/SBA-15 synthesized using a conventional impregnation method was used as a reference sample. These Sn-modified materials were used as supports for Pt-based catalysts and tested in propane dehydrogenation. The differences among the samples in terms of structure-activity relationships were identified and discussed. The conclusions were used to explain the specific catalytic properties.

2. Experimental

2.1. Catalyst preparation

The Sn-modified mesoporous SBA-15 material was prepared using a one-pot hydrothermal method. In a typical procedure, a triblock copolymer (2 g, P123, $EO_{20}PO_{70}EO_{20}$, Aldrich) was dissolved in HCl (60 mL; 2 mol/L) and deionized water (15 mL). A calculated amount of $SnCl_2{\cdot}2H_2O$ (Aldrich) was added. The mixture was stirred at 40 °C for 3 h. Tetraethyl orthosilicate (4.25 g, 98%) was added dropwise and the mixture was stirred for 24 h. The resulting suspension was crystallized in a Teflon-lined autoclave at 100 °C for 24 h. The mixture was filtered, and the residue was washed and dried at 80 °C for 12 h, and calcined in air at 550 °C for 6 h. The obtained samples were denoted by *x*Sn-SBA-15 (nominal Sn mass fraction *x* wt% = 0, 0.5, 1, and 2 wt%). Another sample was synthesized using an incipient wetness impregnation (IM) procedure and denoted by *x*Sn/SBA-15-IM.

The Pt-based catalysts were prepared using an incipient wetness impregnation method. The support powder was impregnated with a $H_2PtCl_6{\cdot}6H_2O$ precursor dissolved in deionized water. After sonication for 30 min, the mixture was rested for 12 h. The solution was dried at 60 °C for 12 h and calcined in air at 500 °C for 4 h. The nominal Pt content of these catalysts was 1 wt%.

2.2. Catalyst characterization

N_2 adsorption-desorption isotherms were recorded at −196 °C using an automated surface area and pore size analyzer (Quadrasorb SI). Before each measurement, the samples were outgassed for 3 h under vacuum at 300 °C. X-ray diffraction (XRD) patterns were recorded at 2θ = 0.5°–10° using an Empyrean diffractometer with Cu K_α (45 kV, 50 mA) radiation.

Fourier-transform infrared (FT-IR) spectra were recorded ate room temperature using a Bruker Tensor 27 FT spectrometer. The spectra were recorded in the range 4000–400 cm^{-1} and KBr was used as the background. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were recorded using a Shimadzu UV-vis-near IR spectrophotometer (UV-3600). The NMR spectroscopic studies for Sn-SBA-15 samples were carried out on a Bruker Avance III 500 spectrometer.

X-ray photoelectron spectroscopy (XPS) was performed using an XSAM800 spectrometer with an Al K_α ($h\nu$ = 1486.6 eV) X-ray source; the C 1*s* binding energy at 284.6 eV was used as an internal standard.

The Sn loadings on the samples were determined using inductively coupled plasma atomic emission spectroscopy (TJA IRIS Advantage spectrometer).

Temperature-programmed H_2 desorption (H_2-TPD) was performed using a Quantachrome Autosorb-1 instrument equipped with a thermal conductivity detector. The catalyst (100 mg) was reduced in situ at 500 °C for 1 h under a 10%H_2-90%N_2 mixture at a flow rate of 30 mL/min. The catalyst was cooled to 30 °C after saturation with H_2 and then purged for 3 h to remove H_2 in the gas phase. The TPD profiles were recorded from 30 to 800 °C at a ramping rate of 10 °C/min.

Scanning electron microscopy (SEM) was performed using a JEOL JSM-7500F instrument at an applied voltage of 10 kV. Transmission electron microscopy (TEM) was performed using a JEOL JEM 2010 electron microscope operated at 120.0 kV. The samples were suspended in ethanol by ultrasonication. Drops of the suspension were dispersed on a copper grid.

Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer. The samples were heated