Article

PtSnNa/SUZ-4: An efficient catalyst for propane dehydrogenation

Hualan Zhou [a], Jingjing Gong [a], Bolian Xu [a], Shengcai Deng [a], Yuanhua Ding [b], Lei Yu [a,b,*], Yining Fan [a,#]

[a] *Key Laboratory of Mesoscopic Chemistry of MOE, Jiangsu Provincial Key Laboratory of Nanotechnology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210046, Jiangsu, China*

[b] *Jiangsu Key Laboratory of Environmental Material and Environmental Engineering, School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, Jiangsu, China*

ARTICLE INFO

ABSTRACT

The structure and catalytic properties of PtSn catalysts supported on SUZ-4 and ZSM-5 zeolite have been studied by using various experimental techniques including XRD, nitrogen adsorption, NH_3-TPD, TG, H_2-TPR and TPO techniques combined with propane dehydrogenation tests. It has been shown that SUZ-4-supported PtSnNa (PtSnNa/SUZ-4) was determined to be a better catalyst for propane dehydrogenation than conventional catalysts supported on ZSM-5, owing to its higher catalytic activity and stability. Dibenzothiophene poisoning experiments were performed to investigate the detailed structures of the two supported catalysts. The characterization of the two catalysts indicates that the distribution of Pt on the porous support affects the activity. In contrast to ZSM-5-supported catalysts, Pt particles on the PtSnNa/SUZ-4 are primarily dispersed over the external surface and are not as readily deactivated by carbon deposition. This is because that the strong acid sites of the SUZ-4 zeolite evidently prevented the impregnation of the Pt precursor H_2PtCl_6 into the zeolite. In contrast, the weak acid sites of the ZSM-5 zeolite led to more of the precursor entering the zeolite tunnels, followed by transformation to highly dispersed Pt clusters during calcination. In the case of the PtSnNa/ZSM-5, the interactions between Sn oxides and the support were lessened, owing to the weaker acidity of the ZSM-5 zeolite. The dispersed Sn oxides were therefore easier to reduce to the metallic state, thus decreasing the catalytic activity for hydrocarbon dehydrogenation.

1. Introduction

It is well reported that supported bi-component Pt-Sn catalysts can be employed in many reactions, including alkane dehydrogenation [1–3], hydrocarbon rearrangement [4], low temperature carbon monoxide oxidation [5], and alcohol electro-oxidation [6]. Among these applications, propane dehydrogenation is considered to be one of the most important petrochemical processes because of the rapidly growing demand for propylene [2,7–9]. Supported Pt-Sn catalysts have been widely used because of their high activities and environmentally friendly characteristics [1,2]. Aluminium oxide (Al_2O_3) is the most common support for these materials, owing to its high surface area and acidity. However, Al_2O_3-supported Pt-Sn cata-

lysts are deficient in terms of poor stability and lack of durability during recovery [1,10,11]. Thus, the development of novel supports to improve the stability of these catalysts is not only highly desirable but also timely.

In recent years, zeolites such as SUZ-4 and ZSM-5 have been found to be good supports because of their high surface areas, good thermal stabilities, large pore volumes and tunable acidity [12–14]. SUZ-4 is a new type of synthetic zeolite patented by the British Petroleum Company in 1992. In the three dimensional topological structure of this material, straight ten-membered channels intersect with two eight-membered channels at an angle of approximately 74°, which is similar to the structure of ZSM-5 zeolite [15,16]. SUZ-4-supported catalysts have been widely used in many processes, such as the conversion of *n*-hexane [16], the synthesis of dimethyl ether from methanol [17], and the elimination of nitrogen oxides [18]. However, there have not yet been any reports concerning the application of SUZ-4-supported catalysts to propane dehydrogenation, while ZSM-5-supported catalysts have attracted significant attention in this regard [13,19]. In contrast to γ-Al$_2$O$_3$, the three-dimensional microporous ZSM-5 zeolite has a well-defined, ten-membered, ring-crossed channel system that prevents the formation of large hydrocarbon molecules, thus improving the catalyst's stability [13]. Recently, Zhou's group [20] investigated propane dehydrogenation over ZSM-5-supported Pt-Sn catalysts and found that the propylene selectivity was significantly improved by introducing promoters to neutralize the support acidity. The addition of hydrogen to the reaction system effectively inhibited the cracking of propane to C1 and C2 products and also reduced carbon deposition on the catalyst surface, thus improving both the dehydrogenation selectivity and catalytic stability [21]. Despite this, the ZSM-5-based catalysts were still easily deactivated by carbon deposition under the chosen reaction conditions. To resolve this issue, our own group developed the SUZ-4-supported catalyst PtSnNa/SUZ-4, which afforded a 20% propylene yield. Although propylene can be obtained in similar 18%–23% yields by increasing the Sn loading when using a PtSn/ZSM-5 catalyst [22], our catalyst has the advantage of being more robust and undergoing very little deactivation due to carbon deposition.

2. Experimental

2.1. Catalyst preparation

An SUZ-4 zeolite with the molar ratio SiO$_2$/Al$_2$O$_3$ = 21 and a ZSM-5 zeolite with the molar ratio SiO$_2$/Al$_2$O$_3$ = 20 were prepared by methods previously described in the literature [23,24]. In each case, the resulting solid phase was filtered, washed with distilled water several times, dried at 110 °C for 12 h and then calcined at 550 °C for 4 h. This was followed by NH$_4^+$ exchange in aqueous NH$_4$Cl (1 mol/L). H-SUZ-4 and H-ZSM-5 were obtained by calcining the ammonium forms of SUZ-4 and ZSM-5 at 550 °C for 4 h. PtSnNa catalysts supported on either the SUZ-4 or the ZSM-5 zeolite (Pt = 0.5%, Sn = 2.0%, Na = 1.0%) were prepared by sequentially impregnating the

H-SUZ-4 or H-ZSM-5 with an aqueous mixture of H$_2$PtCl$_6$ and SnCl$_4$ (H$_2$PtCl$_6$ = 5 mg/mL, SnCl$_4$ = 5.85 mg/mL) and with aqueous NaCl (0.5 mol/L). The impregnated samples were dried at 110 °C for 4 h, calcined at 520 °C for 4 h, and then dechlorinated in air containing water vapor at 530 °C for 4 h.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of all samples were obtained with a Philips X'pert pro diffractometer using Cu K_α radiation at 40 kV and 40 mA, from 5° to 50°. Surface areas were calculated by the BET method based on N$_2$ adsorption isotherms recorded at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer. The samples were degassed at 300 °C and 0.133 Pa prior to analysis, after which isotherms were acquired at −196 °C. NH$_3$-TPD profiles of the specimens were obtained in a flow-type fixed-bed reactor at ambient pressure. The catalysts were pre-treated at 500 °C for 2 h under an Ar flow. The NH$_3$ adsorption temperature was 100 °C, and the temperature was raised at a rate of 10 °C/min. The desorbed NH$_3$ was detected by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

H$_2$ chemisorption on the supported PtSnNa catalysts was assessed both before and after the propane dehydrogenation reaction according to a previously described procedure [25]. Each of the catalysts was reduced in a H$_2$ flow at 500 °C for 2 h and then out-gassed in an Ar flow at 540 °C for 2 h before H$_2$ chemisorption measurements.

The amount of carbonaceous material deposited on each catalyst during the propane dehydrogenation reaction was measured using thermo-gravimetric (TG) analysis (STA 449C-Thermal star 300 TA-MS apparatus). Catalyst samples (each approximately 0.02 g) obtained after a 10-h reaction were heated from room temperature to 900 °C in O$_2$ (at 25 mL/min) at a heating rate of 10 °C/min, and the amounts of coke on the specimens was calculated from the resulting TG curves.

Temperature-programmed oxidation (TPO) was determined with the same apparatus as used for the H$_2$ chemisorption experiments. An approximately 0.1-g sample was placed in a quartz reactor and then heated to 800 °C in a mixture of O$_2$ (at 3.0 mL/min) and Ar (at 30 mL/min) at a heating rate of 10 °C/min. Temperature-programmed reduction (TPR) was performed using the same apparatus employed during the TPO assessments. In these trials, approximately 0.1-g samples were placed in a quartz reactor and subsequently heated in a flow of 5% H$_2$-95% Ar (at 20 mL/min) at a heating rate of 10 °C/min.

Purposely poisoned catalysts (containing 0.02% S) were prepared by impregnating the reduced PtSnNa/SUZ-4 or PtSnNa/ZSM-5 catalysts with an ethanol solution of dibenzothiophene (0.2 mg/mL), followed by flushing with nitrogen for 1 to 2 h to evaporate residual ethanol and drying at 110 °C for 4 h.

All catalysts were reduced in H$_2$ at 500 °C for 2 h before catalytic evaluation. The propane dehydrogenation reaction was carried out in a quartz tubular micro-reactor under