



Propane dehydrogenation over PtSnNa/La-doped Al₂O₃ catalyst: Effect of La content

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ABSTRACT

La-doped mesoporous alumina (La-Al) with different content of La was synthesized and then this kind of material was used as the support for platinum–tin catalyst in propane dehydrogenation. It was found that a portion of La had been incorporated into the alumina framework with La-doping. When the content of La in the support was suitable, both the catalyst acidity and the coke amount were decreased. Moreover, in these cases, the presence of La could not only promote the distribution of metallic particles, but also strengthen the interaction between tin species and support. As a result, more amounts of tin could exist in oxidized states, which was beneficial to enhance the interaction of Pt with SnO_x species and the reaction activity. In the current study, the PtSnNa/La-Al catalyst with 1.0 wt.% La exhibited the best catalytic activity and stability. Compared with pure Al₂O₃ support, this La-doped Al₂O₃ support was also favorable for the improvement of the catalytic performance even at higher reaction temperature (605 °C). However, with the excessive addition of La, the agglomerations of metallic particles and the increase in percentage of metallic tin (Sn⁰) on the catalyst were found, which seriously resulted in the deactivation of catalyst.

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1. Introduction

The catalytic dehydrogenation of propane is of increasing importance because of the growing demand for propene [1–3]. Indeed, propene is an important raw material for the production of polypropene, acrolein, polyacrylonitrile and acrylic acid. However, it should be noted that the reaction of propane dehydrogenation is an endothermic process, which requires a relatively high temperature to obtain high yield of propene. Thus, the catalyst deactivation due to coke formation is inevitable. It is the key to develop the catalyst possessing high-activity, high-stability and high-selectivity.

The platinum–tin catalysts have been widely used in reforming or dehydrogenation processes. The role of Sn and addition of several promoters, including alkali metals (Na, K) and rare earth metal (La) to PtSn catalysts has been extensively investigated in many studies [4–9]. Moreover, it has been reported that there exist many factors determining the catalytic performance of the PtSn catalysts, such as the interactions between Pt and Sn, the chemical state of Sn, and the support effect [10–12]. As regards the support, it cannot only modify the selectivity of the process by catalyzing lateral reactions, but also influence the properties of the final metallic phase [4]. An example by He et al. [12] has been proved that the support effect

for Pt–Sn catalyst in the dehydrogenation of long chain paraffin can be divided into the following three parts: (I) the BET and pore size distribution govern the Pt dispersion; (II) the inherent acidity of the support controls the catalyst acidity; (III) the pore volume provides the effective capability for carbon deposition. As a consequence, the development of new support, with a high surface area, a narrow pore size distribution and a high pore volume, has been received a great deal of attention due to its distinctive structure and property [6,11].

Alumina has been used as an adsorbent, catalyst or catalyst support in the automobile and petroleum industry due to its desirable textual properties and surface acid–base properties [13]. Compared to the conventional γ -Al₂O₃, mesoporous alumina (Al₂O₃) has some unique physical properties, such as large surface area, narrow pore size distribution and tunable pore size over a wide range [14]. Furthermore, mesoporous alumina simultaneously possesses the characteristics of the alumina and mesoporous material. In this way, it can be expected that the alumina feature of this material helps to maintain the oxidation state of Sn, while the mesoporous characteristic having a certain pore volume favors the catalytic capacity to accommodate the coke that formed or migrated. These properties make mesoporous alumina as an interesting material for applications as a catalyst carrier for some petrochemical processes. For instance, Shee and his co-workers [15] studied the catalytic performances of mesoporous Cr₂O₃/Al₂O₃ catalysts containing 2–15 wt.% chromia in the dehydrogenation of light alkane. They concluded that the different loading of chromia had an obvious influence on the catalytic activity and the formation of subsurface Cr (III) species might be the reason

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for the permanently lost activity. To further improve the thermal stability and modify the acidic/basic properties of the supports, the incorporation of some metal species into the alumina matrix has been confirmed as an effective method [11]. Vu et al. [16] systematically investigated the role of La-, Ce-, and Y-doped mesoporous alumina in the formation and stability of Pt–Sn alloy during the process of propane dehydrogenation. It was found that La-, Ce-, and Y-doped Al_2O_3 with the same percentages of the rare earth metals (10 wt.%) could not only increase the Pt dispersion, but also decrease the reduction temperature of the Pt–Sn species. However, worthy mention is that in this reported literature, the influences of the different metal concentration on the catalytic performance and stability had not been considered. Actually, the presence of rare earth metal with different content in the support may result in the changes in the catalytic structure, dispersion of metallic particles and metal-support interactions, which can influence the catalytic performances significantly. An in-depth understanding of the metal concentration and the metallic role in the support is helpful to improve the performance of the catalyst for the dehydrogenation of propane.

In the present study, La-doped mesoporous alumina with the different content of La was synthesized and then this kind of material was used as support for platinum–tin catalyst in the dehydrogenation of propane. The catalysts were studied by several techniques, including XRD, nitrogen adsorption, ^{27}Al MAS NMR, TEM, NH_3 -TPD, TPR, XPS, TPO and hydrogen chemisorption. Particular emphasis was focused on the changes of Pt–Sn interaction and character of active sites on the catalyst with the increasing content of lanthanum. All the results were correlated with a corresponding catalytic reaction. This can provide us with important information to understand the role of La in the support on metallic catalyst.

2. Experimental

2.1. Synthesis of the support

La-doped mesoporous alumina (La-Al) was synthesized using the sol–gel method, as described previously [16]. Typically, 6.0 g of cetyl trimethyl ammonium bromide (CTAB) was added to a mixture containing 525 mL of deionized water and 225 mL of ethanol under vigorous stirring at 60 °C for 20 min. The determined amount of $\text{La}(\text{NO}_3)_3$ was added to the solution. About 23.84 g aluminum isopropoxide and 10.2 mL NH_4OH (28%) were added quickly to the solution. The resulting mixture was maintained at 60 °C and continually stirred for 3 h. After filtration, the product was washed with 500 mL ethanol and dried in air at 25 °C for 12 h. The obtained product was calcined in an air flow via heating from room temperature to 550 °C at a ramping rate of 2 °C/min and holding at 550 °C for 6 h. Mesoporous alumina (Al) was similarly synthesized without the addition of lanthanum species and addition of NH_4OH to the solution before aluminum isopropoxide.

2.2. Catalyst preparation

The catalysts were prepared by sequential impregnation method in our experiments. First, the powder of mesoporous alumina (Al) or La-doped mesoporous alumina (La-Al) was impregnated in an aqueous solution of NaCl. Subsequently, Pt and Sn were deposited by co-impregnating H_2PtCl_6 and SnCl_4 aqueous solution, followed by drying. In all cases, the loadings of Pt, Sn and Na were 0.5, 1.0 and 1.0 wt.%, respectively.

Afterwards, the prepared samples were fully agglomerated with binder during the process of pelletization [3]. After totally dried, the catalysts were calcined at 500 °C for 4 h and dechlorinated at 500 °C for 4 h in air containing steam. Catalysts used during this investigation were labeled as PtSnNa/(w)La-Al, where the letter w represented the percentages (wt.%) of La incorporated into Al_2O_3 .

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the different samples were recorded with a Siemens D5000 using nickel filtered $\text{Cu K}\alpha$ radiation. The X-ray tube was operated at 40 kV and 40 mA and an angular range 2θ from 20 to 80° was recorded.

The nitrogen adsorption–desorption isotherms were measured at –196 °C on a Micromeritics ASAP 2000 apparatus. Before measurements, the samples were degassed at 300 °C and 1×10^{-3} Torr. The pore structural data were analyzed by the BJH (Barrett–Joyner–Halenda) method using the Halsey equation for multilayer thickness. The pore size distribution curve came from the analysis of the desorption branch of the isotherm.

Solid-state ^{27}Al MAS NMR spectra were collected in a Bruker DSX-400 spectrometer. The ^{27}Al NMR spectra were obtained at 10.0 kHz, using 15° pulses and 4 s delay, a total of 2000 pulses being accumulated.

TEM studies were analyzed using a JEM-2010 microscope operated at 200 kV. Reduced catalyst samples were prepared by grinding and suspending the catalysts in ethanol, followed by dropping then a small amount of this solution onto a carbon coated copper grid and drying before loading the sample in the TEM. The particle size distribution was obtained by measuring 200 individual metallic particles.

Surface acidity was measured by NH_3 -TPD in TP-5000 apparatus at an ambient pressure. About 0.15 g of sample was placed in a quartz reactor and saturated with ammonia at room temperature. TPD was carried out from 100 °C to 500 °C with a heating rate of 10 °C/min and with helium (30 mL/min) as the carrier gas.

Temperature-programmed reduction (TPR) was measured in the TP-5000 apparatus. Prior to the TPR experiments, the catalysts were dried in flowing N_2 at 400 °C for 1 h. 5% H_2 –95% N_2 was used as the reducing gas at a flow rate of 40 mL/min. The rate of temperature rise in the TPR experiment was 10 °C/min up to 700 °C.

X-ray photoelectron spectra (XPS) measurements were carried out in a Thermo ESCALAB 250 instruments (USA) using non-monochromatic $\text{Al K}\alpha$ 1486.6 radiation. All samples were reduced in situ under hydrogen at 500 °C for 1 h. Then the spectra were recorded at room temperature in a vacuum better than 5×10^{-9} mbar. The binding energies (BE) were referenced to the Al 2p peak, and the BE of which was fixed at 74.5 eV [9].

Hydrogen chemisorption experiment was performed on the apparatus that described for NH_3 -TPD. The measurement was determined by the pulse chemisorption technique using a conventional setup equipped with a temperature controlled setup and TCD detector [17]. The sample (0.2 g) was reduced in flowing H_2 (5 mL/min) at 500 °C for 2 h, then purged in N_2 at 550 °C for 1 h to remove the hydrogen. The catalysts were saturated by hydrogen pulses at 30, 300, and 450 °C. The pulse size was 5 mL of a 5% H_2 –95% N_2 mixture and the time between pulses was 3 min.

Coke was analyzed by thermogravimetric (TG) test and temperature-programmed oxidation (TPO) experiment. Thermogravimetric analysis was measured in air flow (30 mL/min) with a LCT thermogravimetric analyzer (Beijing optical instrument factory, PR China) from room temperature to 700 °C at the rate of 20 °C/min. 0.02 g of the catalyst was set in the analyzer. TPO was measured with the same apparatus as used for TPR. About 0.05 g of sample was placed in a quartz reactor and then heated up to 650 °C at the rate of 10 °C/min in a 5% O_2 –95% He mixture (30 mL/min).

2.4. Catalytic evaluation

The propane dehydrogenation was carried out in a conventional quartz tubular micro-reactor and all the catalysts were reduced in H_2 at 500 °C for 8 h before catalytic evaluation. The catalyst (mass 2.0 g) was placed into the center of the reactor. Reaction conditions were as follows: 590 °C for reaction temperature, 0.1 MPa for total pressure,

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