



Full Length Article

Nature of active tin species and promoting effect of nickle in silica supported tin oxide for dehydrogenation of propane



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ABSTRACT

Different with Wang et al.'s study, we found that polymeric Si–O–Sn²⁺ rather than Ni–Sn alloy and metallic Sn are active species in silica-supported tin oxide catalysts for dehydrogenation of propane. The results showed that high surface area of mesoporous silica brought about high dispersion of tin oxide species, as a result, catalytic activity and stability were both improved. DRUV–vis, XPS, TPR and XRD studies of fresh and reduced catalysts indicated that the deactivation was related to the reduction of active species rather than the coke formation since active tin species cannot maintain its oxidation state at reaction conditions (high temperature and reducing atmosphere). The formed Ni₃Sn₂ alloy after reduction just functioned as promoter which accelerated the desorption of H₂ and regeneration of active site. A synergy effect between active tin species and Ni₃Sn₂ alloy were observed.

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1. Introduction

The demand of propene increased steadily in the past few years on account of its extensive use as feedstock employed in the production of a plenty variety of chemicals. Used in commercial propane dehydrogenation processes at present, Pt- and CrO_x-based catalysts suffer from several issues such as high cost of Pt and chemical contamination related to the use of Cr, in spite of their excellent catalytic performance in propane dehydrogenation. Alternatively, some metal oxides (Gallium oxide, Molybdenum oxide, Iron oxides, Zinc oxide, etc.) which are relatively low cost and low toxicity exhibit high catalytic activity toward dehydrogenation of propane.

Nevertheless, they are susceptible to deactivation because of coke formation and reduction of active sites [1–3]. Therefore, many studies focus on the improvements in catalytic performance especially stability of supported metal-oxides catalysts. In recent work by Sattler et al., a highly active, selective, and stable 1000 ppm of Pt promoted 3 wt% Ga/Al₂O₃ catalyst was obtained [4]. It was suggested that the existence of Pt facilitated the recombination of the hydrogen atoms on the gallium hydride hydroxide species and promoted the regeneration of the active sites. They state that Pt just function as promoter rather than active component. Gong et al. also found that trace amount of platinum (0.1 wt%) significantly improved the catalytic performance of ZnO/Al₂O₃ [5]. These

authors proposed that the incorporation of platinum has multiple function. On the one hand, ZnO was modified as a stronger Lewis acid by platinum due to the electron transfer from the ZnO to the Pt, thus easier C–H breaking was achieved and on the other, Pt accelerated H₂ desorption, as a result, catalyst stability is significantly enhanced.

As the most studied promoter, Sn plays an important role in Pt-based propane dehydrogenation catalysts. The addition of tin modifies not only platinum active phase but also support. As a consequence, the acidity of support was neutralized and side reactions (hydrogenolysis, isomerization, etc.) were suppressed [6–8]. Even though these beneficial effects of tin are widely known and considerable research attempt to explain the mechanism by which tin influences the catalytic properties of platinum, tin was just studied as promoter but not active component in Pt-based catalyst.

In previous work, silica supported Ni–Sn alloy, prepared by co-impregnation method, had been shown to be active in isobutane dehydrogenation [9]. However, in this study, we found that the addition of nickle to the silica supported tin oxide had a negative effect on its activity. With the addition of more nickle, the lower activity was obtained. Besides, this negative effect is also observed in Cu and Co-promoted SnO₂/SiO₂. Onda et al. suggested that it is difficult to obtain the single-phase Ni–Sn alloy on SiO₂ by the co-impregnation method [10]. As a result, the activity of Ni–Sn/SiO₂ may not derive from Ni–Sn alloy but other active species. Recently, Wang et al. also claimed that silica supported metallic Sn was active species in dehydrogenation of propane, but their XPS results of Sn 3d_{5/2} peak assignment are questionable [11]. It was also confusing

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Table 1
BET results for three types of silica.

Sample	$S_{\text{BET}}/(\text{m}^2 \text{ g}^{-1})$	$V_p/(\text{cm}^3 \text{ g}^{-1})$	D_{BJH}/nm
Si-1	288	1.14	14.5
Si-2	416	0.93	7.6
MCM-41	1121	0.82	2.7

that trace amount of Pd (0.05 wt%) can significant inhibit the loss of metallic Sn since Sn is liquid at such high reaction temperature. Consequently, it is unlikely that metallic Sn can be stabilized by such low content of Pd. To our minds, the evaporation of liquid metal Sn may be responsible for its loss during reaction. The similar XPS results are obtained in this work which supported that tin oxide is the active species in propane dehydrogenation rather than metallic tin and Ni-Sn alloy. Therefore, the aim of the present study is to obtain detailed information on the exploration of catalytic behavior, nature of active tin species and how the addition of Ni improves the catalytic properties over silica supported tin oxide.

2. Experimental section

2.1. Catalyst preparation

Three types of mesoporous silica with different specific surface area were used in this study. The details of the silica supports were summarized in Table 1. Si-1 and Si-2 were obtained from China Qingdao Haiyang Chemical Company. MCM-41 was prepared according to procedure described elsewhere [12].

2.1.1. Mesoporous silica supported SnO_2 with different SnO_2 loading

A series of mesoporous silica supported SnO_2 catalysts with different contents were prepared via incipient wetness impregnation of Si-2 with an ethanolic solution containing different amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (obtained from Sinopharm Chemical Reagent Company). The prepared catalysts were dried at 35°C overnight and then calcined at 500°C in air for 3 h ($5^\circ\text{C}/\text{min}$ heating rate). The prepared catalysts were named $x\text{SnO}_2/\text{Si-2}$, where x is the $\text{SnO}_2/(\text{SiO}_2 + \text{SnO}_2)$ weight ratio.

2.1.2. SnO_2 -based catalysts supported on different types of mesoporous silica

Si-1, Si-2, and MCM-41 mesoporous silica were used as support. The catalysts were prepared with the same protocol as described in 2.1.1. The prepared catalysts were named as $x\text{SnO}_2/\text{Si-1}$, $x\text{SnO}_2/\text{Si-2}$ and $x\text{SnO}_2/\text{MCM-41}$, respectively.

2.1.3. Metal (Ni, Co, and Cu) promoted silica-supported SnO_2

Metal (Ni, Co, and Cu) promoted $\text{SnO}_2/\text{SiO}_2$ catalysts were prepared by impregnating the post-synthesized $\text{SnO}_2/\text{Si-2}$ catalysts with ethanolic solution containing different amount of its metal nitrate precursors ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (obtained from Sinopharm Chemical Reagent Company). The prepared catalysts were dried at 35°C overnight and then calcined at 500°C in air for 2 h ($5^\circ\text{C}/\text{min}$ heating rate). The samples are denominated hereafter according to the metal precursor used, i.e., $x\text{Ni } y\text{SnO}_2/\text{Si-2}$ corresponds to a material prepared using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor, where x, y are Ni and SnO_2 loading, respectively.

2.2. Characterization

Temperature-programmed reduction (TPR) was performed under flowing 5 vol% H_2/N_2 to examine the reduction behavior of the catalysts stored in air. 50 mg (40–60 mesh) samples were

heated under helium (30 ml/min) from room temperature to 500°C and maintained for 1 h in order to remove the adsorbed carbonates and hydrates. After cooling down to room temperature, the gas was switched to 5 vol% H_2/N_2 (30 ml/min). The temperature of the sample bed was raised from room temperature to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ and the signal of hydrogen consumption was registered with a thermal conductivity detector. H_2 Chemisorption was carried out using a dynamic pulse technique (Micromeritics Autochem 2950 HP) to quantify the reduction extent of the catalysts at 500°C . A loop with known volume was pulsed over the catalyst and the H_2 consumption was monitored with thermal conductivity detector. In order to investigate carbon contents in used catalysts, a high-frequency infrared carbon sulfur analyzer (HX-HW8B) was employed. The samples were heat-treated at 1000°C in oxygen atmosphere and the obtained carbon dioxide was quantified by infrared analyzing instrument. The structure of samples was analyzed by powder X-ray diffraction (Rigaku D/Max RB) with $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The measurements were performed with 2θ values between 10° and 75° with a scanning speed of $10^\circ/\text{min}$. The BET surface area and pore structure was measured by the BET method at -196°C on a Micromeritics TriStar3000 apparatus. X-ray photoelectron spectra (XPS) analysis was recorded on a Thermo Fisher Scientific K-Alpha apparatus equipped with an Al $\text{K}\alpha$ monochromator X-ray source. The UV-vis diffuse reflectance spectra were recorded by a Shimadzu UV-2700 spectrophotometer.

2.3. Catalytic tests

Catalytic tests were carried out in a fixed-bed reactor. Prior to catalytic experiment, all the catalysts were heated to 500°C from room temperature ($5^\circ\text{C}/\text{min}$ heating rate) with 5 vol% H_2/N_2 (100 ml/min), and kept at 500°C for 1 h. After the catalysts were reduced, the reactor was flushed with inert gas in order to remove residual hydrogen before switching to the reactant and the temperature was raised to 580°C simultaneously. Reactant which consists of 99.9 wt% propane was introduced into the reactor and the dehydrogenation of propane was carried out under atmospheric pressure. The weight hourly space velocity (WHSV) of propane was 0.65 h^{-1} . The product gas was analyzed by Bruker GC-450 chromatography which equipped with a FID detector. The propane conversion and propene selectivity were calculated from the total number of carbon atoms balance.

The deactivation parameter was calculated by the following equation:

$$k_d(\text{h}^{-1}) = \frac{\ln\left(\frac{1-X_{\text{end}}}{X_{\text{end}}}\right) - \ln\left(\frac{1-X_{\text{start}}}{X_{\text{start}}}\right)}{t}$$

where X_{start} and X_{end} refer to the conversion at the start and the end of an experiment, and t is the reaction time of the experiment in hours. Hence, the higher k_d values mean lower stability.

3. Results and discussion

The XRD patterns of fresh $x\text{SnO}_2/\text{Si-2}$ catalysts containing different amount of SnO_2 are presented in Fig. 1. The major diffraction peaks with 2θ values of 26.5° , 33.9° and 51.7° are assigned as the characteristic peaks of SnO_2 phase with the tetragonal rutile structure and the broad peak at 22.27° corresponding to the amorphous nature of silica [13]. Additionally, the peak intensity of $x\text{SnO}_2/\text{Si-2}$ catalysts strengthen with the increasing loading of SnO_2 and no diffraction peaks of SnO_2 are detected until its content less than 1.5 wt%. Moreover, the XRD patterns of SnO_2 supported on different mesoporous silica are compared (Fig. 2). The $6.5\text{SnO}_2/\text{MCM-41}$ indicates very weak and broad peaks of SnO_2 phase whereas it is sharp and narrow in $6.5\text{SnO}_2/\text{Si-1}$ and $6.5\text{SnO}_2/\text{Si-2}$, implying a

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