Chemical Engineering Journal 278 (2015) 240–248

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Effect of steam addition on the structure and activity of Pt–Sn catalysts in propane dehydrogenation

Yuling Shan [a], Zhijun Sui [a,*], Yian Zhu [a], De Chen [b], Xinggui Zhou [a]

[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China
[b] Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

## HIGHLIGHTS

- Both promoting and retarding effects of steam are observed.
- Twofolds of activity are obtained by introducing certain amount of steam.
- Propane hydrogenation in steam has lower activation energy.
- Segregation of Pt over Pt–Sn surface is observed in steam environment.

## ARTICLE INFO

*Article history:*
Available online 13 October 2014

*Keywords:*
Propane dehydrogenation
Platinum–tin
Steam pretreatment

## ABSTRACT

To investigate the role of steam on the structure and activities of platinum-based catalyst, a tin modified Pt/γ-$Al_2O_3$ catalyst was prepared for propane dehydrogenation in the presence of steam. The propane conversion could be prominently elevated by nearly twofolds with only 1.0% loss of selectivity to propene when an optimum amount of $H_2O$ was added. The retarding effects of steam on the activities are also observed at higher $H_2O/C_3H_8$ molar ratios (>1). Kinetic studies results show that the apparent activation energies for steam dehydrogenations are lower than those without steam addition. The fresh, spent and steam pretreated catalysts were characterized by TG, Raman, $H_2$-chem, HAADF-STEM, XPS and CO adsorption FT-IR (CO-FTIR). It is observed that the platinum particles sizes are smaller in the samples subjected to certain period of steam pretreatment. The changes of platinum dispersion in steam conditions are related to the changes of tin oxidation states and the segregation of platinum from Pt–Sn alloys, as revealed by CO-FTIR and XPS results. More accessible Pt sites that are generated in the steam due to the phase transformation of Pt–Sn catalyst as well as the removal of coke accumulated on the catalyst surface would account for the increase of catalytic activities and the decrease of activation energies in steam atmosphere. Competitive adsorption of $H_2O$ and other reagent over Pt sites would lead to the retarding effects of steam on the activities at high $H_2O$ partial pressure.

## 1. Introduction

Propane is one of the most important building blocks for a wide array of commodity and specialty chemicals. Traditional ways of producing propene like steam cracking of petroleum-derived naphtha, now cannot meet the increasing demand in worldwide market. The alternative way of producing propene via dehydrogenation from propane, which is a naturally abundant source, is becoming more and more important to capture the marginal, additional capacity needed to compensate for the imbalance of propene market [1–3].

The most promising catalysts used in propane dehydrogenation process are platinum based catalysts, with tin as promoters to further promote catalytic activity, selectivity and stability [4–6]. To achieve reasonably industrial interested per-pass conversion, this intrinsic highly endothermic process is usually operated at high temperatures to conquer thermodynamic limitations [2]. However, this would lead to cracking and coking by-products, thus requiring repeated catalysts regenerations [1,7,8]. Some techniques were proposed to improve this process, including oxidative dehydrogenation [9–12], steam dehydrogenation [13], hydrogen removal by selective oxidation [14] or by membrane [15–17]. From the point of view of thermodynamic, steam is a good medium to elevate propane equilibrium conversion by lower propane partial pressure. Steam can also be served as heat carrier and coke remover to

---

* Corresponding author.
*E-mail address:* zhjsui@ecust.edu.cn (Z. Sui).

http://dx.doi.org/10.1016/j.cej.2014.09.107
1385-8947/

elongate the catalysts' activity [18]. Steam could be generated in hydrogen combustion reactor and enter the following dehydrogenation reactors if selective hydrogen oxidation process is incorporated in the processes. In addition, steam also present in catalysts regeneration process. Therefore, it is important to investigate the role of steam on the structure and activities of platinum based catalyst.

Very few investigations have reported the effects of steam on propane dehydrogenation process and some contradictive conclusions were seen in the literature [3]. Kogan et al. [19,20] found that dehydrogenation rates were higher in presence of steam than that in hydrogen atmosphere over their modified Pt/$\theta$-$Al_2O_3$ and Pt/corundum catalysts. They supposed that hydroxyl was involved in the rate limiting step thus promoting the dehydrogenation process. Similar hydroxyl involved model was also accepted by Fattahi et al. [21] to understand their observed higher propane conversion in presence of certain amount of steam over a commercial Pt–Sn–K/$\gamma$-$Al_2O_3$ catalyst. However, retarding effects of steam was observed by Luu et al. [22] over tin modified Pt/$\gamma$-$Al_2O_3$, and steam was involved in the dominator of their kinetic model with a second order. Similar decrease of initial catalytic activity effects of steam was also observed by Dong et al. [23] and sintering of platinum particles was supposed to account for the observed activity decrease. Dong et al. [24] also reported better performance of Pt–Sn/$MgAl_2O_4$ and Pt–Sn/$ZnAl_2O_4$ could be obtained in steam atmosphere and they supposed that the steam modified catalyst's surface was responsible for the phenomena. It seems that the catalytic performances in presence of steam were closely related to the specific catalysts under investigation. But the relationship between the structure of catalysts and catalysts' performances still needs further exploration.

In the present study, a tin modified platinum catalyst was prepared and tested as catalyst for propane dehydrogenation under different steam partial pressures. The catalysts were characterized by using TG, Raman, $H_2$-chem, HAADF-STEM, XPS, CO-FTIR techniques. Finally, the changes of catalysts properties and their relationship with their activities were discussed.

## 2. Materials and method

### 2.1. Preparation of catalysts

A $\gamma$-$Al_2O_3$ was used as support to prepare Pt–Sn catalysts, which was obtained by calcinating pseudo-boehmite at 600 °C for 8 h in air. Bimetallic Pt–Sn/$\gamma$-$Al_2O_3$ catalyst, with the loading of 0.5 wt.% Pt and 3.0 wt.% tin, was prepared by sequential incipient impregnation method. The alumina support was firstly impregnated with an aqueous solution of $SnCl_4{\cdot}5H_2O$ (99.0%, Sinopharm). The tin containing liquid was added dropwise with stirring, followed by aging at room temperature for 12 h, drying at 120 °C for 8 h and calcination at 500 °C for 3 h with a heating rate of 1 K/min. After that, the sample was impregnated with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (99.9%, Sinopharm)) by using the same procedure for supporting tin. A supported Pt catalyst without tin was also prepared by a similar method.

### 2.2. Characterization of catalysts

The amounts of coke formed on the spent catalysts were determined by TG (thermal gravimetric) analysis (SDT Q600, TA Company, USA) in air. Raman analysis was performed at room temperature under ambient conditions on a via-Reflex Raman spectrometer (Renishaw), equipped with a 514.5 nm Ar-ion laser beam. $H_2$ adsorption characterizations were carried out on ASAP 2020 (Micromeritics, USA). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a Tecnai G2 F20 S-Twin equipped with digitally processed STEM imaging system. The XPS spectra were obtained with a VG ESCALAB 200R spectrometer equipped with a hemispherical electro analyzer and a Mg K$\alpha$ 120 W X-ray source. FT-IR spectra were collected by using a Perkin Elmer Spectrum 100 spectrometer equipped with a MCT detector. The spectrum was collected at a resolution of 4 $cm^{-1}$ and in the wavenumber range of 6000–400 $cm^{-1}$. All FT-IR measurements were performed at room temperature (RT) on self-supported pellets contained in a gold sample holder of IR cell with ZnSe windows.

### 2.3. Catalytic performances and kinetic studies

The propane dehydrogenation reaction was carried out in a μBenchCAT reactor (Altamira Instrument, USA) equipped with quartz reactor with a inner diameter of 6 mm. The reactor was placed in an electrical furnace and the reaction temperature could be maintained within ±0.5 °C of the desired set point. The catalyst loading was 0.1 g for catalytic performances experiments over PtSn/$\gamma$-$Al_2O_3$. All the experiments were conducted at $WHSV_{propane} = 14.7\ h^{-1}$ and a hydrogen to propane molar ratio of 0.8. The water was introduced into the reactor system by using a pump and vaporized before reaching the reaction zone. Varying amount of steam was introduced during experiment and is indicated by $H_2O/C_3H_8$. Argon was used as balance gas to get a total flow of 76.15 ml/min. Kinetic experiments were carried out at temperatures ranging from 818 K to 878 K with the same total flow and catalyst loading as above, at which conditions mass transfer limitations were excluded. The gas compositions ($C_1$–$C_3$ hydrocarbons, $H_2$, CO and $CO_2$) were analyzed online with a 4-channel Micro-GC(INFICON 3000, USA).

### 2.4. Steam pretreatment

The fresh reduced samples were pretreated in steam at 773 K for 0, 15, 60 and 180 min, and denoted as PtSn-0, PtSn-15, PtSn-60 and PtSn-180, respectively. The steam partial pressure was kept at 17.3 kPa for all samples. Before exposure to ambient air, the fresh reduced and steam pretreated samples were passivated in flowing 0.5% $O_2$/Ar (5 $cm^3g^{-1}s^{-1}$) for 1.5 h at 293 K.

## 3. Results

### 3.1. Propane dehydrogenation in presence of steam

The catalytic performances of PtSn/$\gamma$-$Al_2O_3$ for propane dehydrogenation at 848 K in the presence of different amount of steam are shown in Fig. 1. As can be seen from Fig. 1(a), the catalytic activities are greatly enhanced when steam is introduced. The conversion of propane increases from 19.0% to 24.9% when the $H_2O/C_3H_8$ mole ratio increases from 0 to 0.5, and further increases to 35.5% at a $H_2O/C_3H_8$ ratio of 1.0. However, any further increasing the amount of steam would only lead to the loss of catalytic activities. In all runs, the catalytic activities decline with TOS. But the deactivation extent, defined as the catalytic activity relative to the initial one, is slower in the presence of steam.

The selectivity to all the gas phase products are shown in Fig. 1(b)–(d). It can be seen that the selectivity to $C_3H_6$ drops slightly in the presence of steam. With the introduction of steam, cracking products and carbon oxides are detected as by-products. The selectivity to these products increases with the increase of steam content while decreases with the increase of TOS. The variations of catalytic selectivity with steam partial pressure as well as