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## Effect of air addition on the catalytic performance of Pt-Sn/ $\text{Al}_2\text{O}_3$ catalysts in propane dehydrogenation

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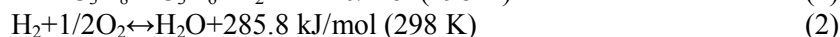
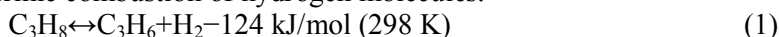
**Abstract.** The  $\text{Al}_2\text{O}_3$ -supported Pt-Sn catalysts were prepared utilizing an impregnation-reduction method and applied in the propane dehydrogenation in the presence of air. The addition of air, it not only provides a part of the heat required by dehydrogenation, but also improves the reaction conversion through the consumption of  $\text{H}_2$  to  $\text{H}_2\text{O}$ . Moreover, the operating conditions of the dehydrogenation process with air have been investigated. The reasonable operating conditions are recommended as follows: temperature=590 °C, GHSV=5200  $\text{h}^{-1}$ , and  $\text{C}_3\text{H}_8$ : air:  $\text{H}_2$ =4:5:4 (molar ratio). Under these conditions, the propane conversion and the propene selectivity attain 39.6% and 96.7%, respectively, simultaneously with the stable catalytic activity.

### 1. Introduction

Propene is an important petrochemical raw material, can be used to produce a variety of chemical products. Traditionally, it is predominantly obtained as a byproduct from steam cracking of naphtha and fluid catalytic cracking, and its yield is subject to the production of ethylene and refined oil [1, 2]. With the growing of demand for propene, the propane dehydrogenation, known as PDH, is an alternative process and has become an important way to increase production of propene [3, 4]. Catalytic dehydrogenation of propane involves the breaking of two carbon-hydrogen bonds to form corresponding propene and hydrogen, as illustrated by equation (1). It is a highly endothermic reaction and accompanied by volume expansion. According to Le Chatelier's principle, higher reaction temperature and/or lower propane partial pressure is used to obtained reasonable propane conversion and propene yield. Additionally, this process is also limited by the thermodynamic equilibrium [5]. To overcome the thermodynamic constraints, the high operating temperature is employed in the propane dehydrogenation. It is generally known that the  $\text{Al}_2\text{O}_3$  supported Pt-Sn has been widely applied as catalyst and commercialized in the dehydrogenation of propane [3, 6]. Pt-Sn/ $\text{Al}_2\text{O}_3$  has high activity and selectivity for propane dehydrogenation. However, the Pt-Sn catalyst still need frequent regeneration due to coke deposition and deactivation. The high temperature of both the dehydrogenation and regeneration process is likely to induce the sintering of the Pt particles, and thus generate small molecular products and coke [4]. As a result, great efforts have been made to improve the dehydrogenation performance of the supported Pt-Sn catalysts by improving the process.



From equation (1), it is possible to shift the reaction equilibrium toward the side of the propene by reducing the partial pressure of propane or by withdrawing the hydrogen formed during dehydrogenation. Low propane partial pressure can be realized through reducing the feed pressure below atmospheric or diluting the feed with steam [7, 8]. Hydrogen can be removed by addition of an oxygen-containing gas by the selective reaction of the hydrogen with the oxygen, as shown equation (2). From equations (1) and (2), it can be seen that the energy consumption of dehydrogenation process can be reduced by the exothermic combustion of hydrogen molecules.



The removal of the hydrogen can be achieved through different strategies in open literature [9-12]. One of the methods is that the reactant is first passed to the dehydrogenation (DH) reactor, and then the dehydrogenation product is fed into the second reactor to carry out selective hydrogen combustion (SHC) [9]. The SHC catalytic systems can also use oxides of the metal Sb, W or Bi on silica or zirconia, and mixed metal oxides such as  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  or  $\text{In}_2\text{Mo}_3\text{O}_{12}$  [10]. Another method is that an oxygen-containing stream is supplied to the reaction medium, the mixtures are then fed to the next reactor in which SHC and DH of unreacted alkane occur at the same time in a common reaction zone. This process is also termed DH-(SHC-DH) model [11, 12]. The third strategy is to use the solid oxygen carrier (such as ceria) react to hydrogen to shift the equilibrium during the process of catalytic dehydrogenation [13]. The advantage in this mode is not supplying elemental oxygen and relatively safe, but the cyclic process is required to regenerate the solid oxygen carrier. However, some people have direct added the oxygen-containing gas to the catalytic dehydrogenation process to improve the yield of olefin and simplify the process [14-16]. In this investigation, Pt-Sn/ $\text{Al}_2\text{O}_3$  catalyst was prepared utilizing the impregnation-reduction method [17] and used in the propane dehydrogenation with  $\text{H}_2$  and air, the effect of air addition and reaction conditions were studied.

## 2. Experimental

### 2.1. Catalyst preparation

The Pt-Sn/ $\text{Al}_2\text{O}_3$  catalyst was prepared using the impregnation-reduction method. Generally, a certain amount of polyvinylpyrrolidone (PVP) was weighed and dissolved in deionized water, then the 8 ml of  $\text{H}_2\text{PtCl}_6$  aqueous solution ( $7.72 \times 10^{-3}$  mol/L) was added in. Next, the 3 g of  $\gamma\text{-Al}_2\text{O}_3$  support, which BET specific surface area, the pore volume and average pore diameter are  $241 \text{ m}^2\cdot\text{g}^{-1}$ ,  $0.54 \text{ cm}^3\cdot\text{g}^{-1}$  and 6.29 nm, respectively, was added quickly to the mixtures. After stirred for 1 h, the sodium borohydride ( $\text{NaBH}_4$ ) in aqueous solution as the reducing agent was slowly added into the suspension liquid and the mixtures were stirred for 4 h. During this time, the suspension liquid gradually varied from milky white to grey black. Afterwards, Sn was deposited on  $\text{Al}_2\text{O}_3$  by impregnating  $\text{SnCl}_2$  ethanol solution, followed by reduced by  $\text{NaBH}_4$  aqueous solution. Finally, the mixed liquid was stabilized for about 0.5 h. After filtrated and washed, the sample was dried at  $120^\circ\text{C}$  for 10 h and then calcined at  $500^\circ\text{C}$  for 4 h. In all the experiments, the molar ratio of PVP:  $\text{NaBH}_4$ : Sn: Pt was 15:15:1.5:1, and the loading amount of Pt and Sn was 0.4 wt% and 0.36 wt% (mass fraction), respectively.

### 2.2. Propane dehydrogenation reaction

The dehydrogenation of propane was carried out at atmospheric pressure in a MRCS-8007 continuous fixed-bed microreactor, which consisted of gas cylinder, automatic flow control system, reactor, and on-line chromatograph analysis system with automatic sampling. The reactor was placed in a heating furnace with 80 mm in the constant temperature zone, and its temperature was controlled using internal thermocouple. The catalyst filling amount was 1.5 g in all cases. The flow rates of  $\text{C}_3\text{H}_8$ ,  $\text{H}_2$  and air were automatically controlled using the mass flow meters. Research has shown that the mixtures of propane and air are flammable at the volume ratios of propane to oxygen ranging from 0.1 to 0.49. According to the literatures [18, 19], the explosion scope could be avoided in the cases of both the volume ratios of propane to oxygen, and hydrogen to oxygen being larger than 1.0. Therefore, the

all experiments were performed outside of the flammability limits. Before the reaction, the catalyst was reduced at 500 °C for 2 h, then the reactor was heated to the reaction temperature and mixed gas containing propane, hydrogen and air as raw materials was let in. The sample analysis was performed 25 min later with the sampling interval of 20 min. The reaction products were analyzed through the combination of two sets of on-line gas chromatographs SP-2100 equipped with TCD detectors. The gas chromatographs equipped with Al<sub>2</sub>O<sub>3</sub> and TDX-01 packed columns which were used to detect CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>+ etc., and O<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>, respectively. The contents of the components were determined by combining the external standard method with the normalization method. The propane conversion ( $X_{C_3H_8}$ ), propene selectivity ( $S_{C_3H_6}$ ), and selectivity of carbon oxygen compounds ( $S_{CO_x}$ ) were calculated according to equations (3)-(5), while the carbon balance was calculated based on equation (6).

$$X_{C_3H_8} = \frac{\sum_i n_i [F_i]_{out} - 3[F_{C_3H_8}]_{out}}{\sum_i n_i [F_i]_{out}} \times 100\% \quad (3)$$

$$S_{C_3H_6} = \frac{3[F_{C_3H_6}]_{out}}{\sum_i n_i [F_i]_{out} - 3[F_{C_3H_8}]_{out}} \times 100\% \quad (4)$$

$$S_{CO_x} = \frac{\sum_i [F_{CO_x}]_{out}}{\sum_i n_i [F_i]_{out} - 3[F_{C_3H_8}]_{out}} \times 100\% \quad (5)$$

$$Carbon\ balance = \frac{\sum_i n_i [F_i]_{out}}{3[F_{C_3H_8}]_{in}} \times 100\% \quad (6)$$

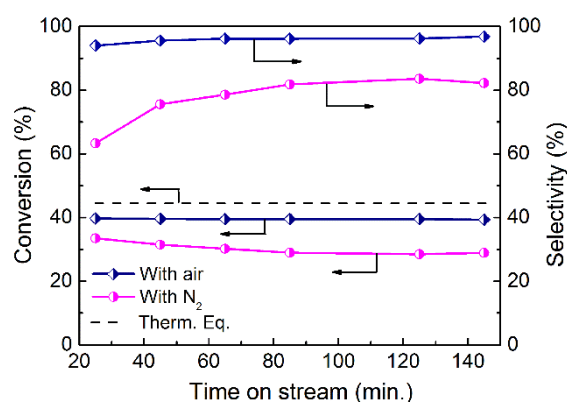
In which,  $[F_i]_{out}$  and  $[F_i]_{in}$  refer to the molar contents of the component  $i$  in outlet and inlet gases, respectively;  $n_i$  is the carbon atomic number contained by the component  $i$ . It was calculated that the carbon balances were 95±5% for all of.

### 3. Results and discussion

#### 3.1. Effect of air-adding

The effects of air addition on the catalytic performance of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst were studied. In order to keep the consistent condition of space velocity, the nitrogen was used as balance gas to get a total gas hourly space velocity (GHSV) of 5200 h<sup>-1</sup>. The catalytic performances of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst for propane dehydrogenation in presence of certain amount of hydrogen or air are shown in Figure 1. As can be seen from Figure 1, the presence of air greatly changes the catalytic performance. It can be seen that the relatively poor reaction activity and stability are obtained in the nitrogen-containing atmosphere. The initial conversion is 35.46%, and the selectivity of propene is only 63.32%. After reaction for 145 min, the conversion decreases from 35.46% to 28.89%, but the selectivity to propene increases progressively from 63.32% to 82.21%. It is well known that the high temperature is required to obtained high propene yields, which is also favorable for the formation of coke. In this case, the active sites of the catalyst can be gradually covered by the coke with the time on stream and result in the decrease of conversion. Besides, it can be speculated that the active centers for the cracking and coking reaction are also decreased, so it cause the increase of selectivity to propene. In contrast to this, the introduction of a certain amount of air into the feed improves the reaction activity and stability significantly. The presence of air promotes the initial conversion of propane to 39.7%,

which is closer to the thermodynamic equilibrium conversion [4], while the propene selectivity is 96%. The analytical results of the dehydrogenation products generated at 85 min are displayed in Table 1.



**Figure 1.** Effects of the air addition on propane dehydrogenation (Reaction conditions: total GHSV=5200 h<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>:air:H<sub>2</sub>=4:5:4, T=590 °C).

**Table 1.** The reaction products of propane dehydrogenation at the different inlet gas composition.

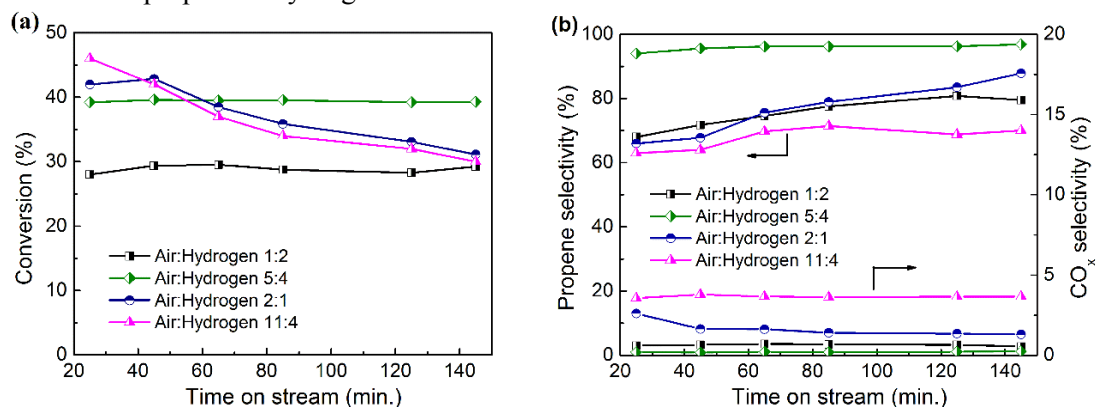
Substrate	Products (%)						Conversion of propane (%)	Selectivity of propene (%)	Yield of propene (%)
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	CO <sub>x</sub>	C <sub>4+</sub>			
C <sub>3</sub> H <sub>8</sub> , H <sub>2</sub> , air	0.51	1.84	39.48	37.69	0.26	0.14	39.48	96.16	38.00
C <sub>3</sub> H <sub>8</sub> , H <sub>2</sub> , N <sub>2</sub>	1.39	3.96	28.48	23.31	0	1.05	28.48	83.57	23.80

As shown in Table 1, in the case of the presence of air, the relatively low contents of the C<sub>1</sub> and C<sub>2</sub> in the products are observed, and only a small number of CO<sub>x</sub> molecules are detected as by-products, meaning that cracking and coking reaction is difficult to take place. This result is mainly related to the high temperature steam generated by the reaction of the hydrogen and oxygen in the air. The formation of steam is beneficial to improving the conversion of propane by reducing the partial pressure of propane and promoting the movement of the balance towards the product side. Previous studies had shown that the C-H cleavage of a second hydrogen atom of propane molecules, i.e. hydride elimination reaction had been suggested as the rate-limiting step of dehydrogenation reaction of propane [20, 7]. Under the condition of certain steam, the hydroxyl group was formed on the metal Pt active sites, which could boost hydride elimination reaction and improve the reaction conversion [21, 7]. Moreover, it can be noted that the catalytic activity is stable under air present. The propane conversion and propylene selectivity almost remain unchanged in the whole reaction stage. Fattahi et al [16] reported that the steam reforming reaction could occur in the propane dehydrogenation with steam addition, which could reduce the content of carbon deposition on the catalyst and therefore increase the stability of the catalyst. It is clear that the addition of air to the feed display the higher catalytic activity and stability, which suggests that the existence of air with suitable concentration is favorable for the dehydrogenation reaction.

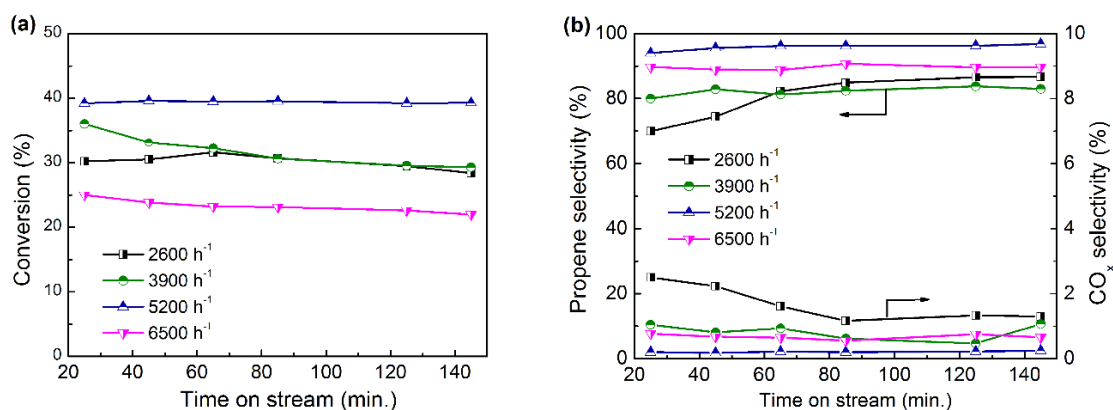
### 3.2. Influence of operating conditions

Figure 2 shows the effect of the different mole ratio of air to hydrogen (air/H<sub>2</sub>) on the catalytic performance of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst in dehydrogenation of propane under a total GHSV of 5200 h<sup>-1</sup> and a constant propane GHSV of 1600 h<sup>-1</sup>. As can be seen from Figure 2(a), the variations of the air/H<sub>2</sub> ratio in the feed have significant influence on the performance in dehydrogenation of propane. With the increase of the air/H<sub>2</sub> ratio, the propane conversion increases, but the stability decreases. The initial conversion of propane increases from 28.0% to 46.2% when the air/H<sub>2</sub> mole ratio increases from 1:2 to 11:4. The highest initial conversion of 46.2% is obtained in the case of the air/H<sub>2</sub> ratio of

11:4, but the deactivation in this case is also fast. With the reaction time prolonged, the conversion decreases to 30.5% after 145 min. The catalytic activities are stable with time on stream when the air/H<sub>2</sub> mole ratio increase from 1:2 to 5:4, but catalytic stability decline when further increasing the air/H<sub>2</sub> ratio. Possible, this behavior may be attributed that the addition of excess air, the amount of steam formed by hydrogen and oxygen reaction increases correspondingly, thus enhancing the competitive adsorption of steam and propane over Pt sites and leading to the decrease of catalytic stability [8]. Moreover, as presented in Figure 2(b), the increasing air/H<sub>2</sub> ratio from 1:2 to 5:4 gives the rapid increase in propene selectivity from 68% to 94%. However, further increasing the ratio of air/H<sub>2</sub> would lead to the decrease of propene selectivity. In contrast to propene selectivity, the CO<sub>x</sub> selectivity exhibits the trends of first decrease and then increase when the air/H<sub>2</sub> ratio increases from 1:2 to 11:4. Obviously, it can be noted that the comparatively lower propene selectivity is obtained when air is over supplied into the feed, which is largely due to the increase of the cracking byproducts including methane, ethane and ethylene, correspondingly increasing the probability of hydrocarbon steam reforming to the CO<sub>x</sub> molecules. With the reaction carrying on, the catalyst presents a favorable stability in the cases of the ratios of 1:2 and 5:4. However, the propene selectivity is low at the air/H<sub>2</sub> ratio of 1:2. Accordingly, it can be concluded that the ratio of 5:4 is suitable to get better catalytic performance for propane dehydrogenation.



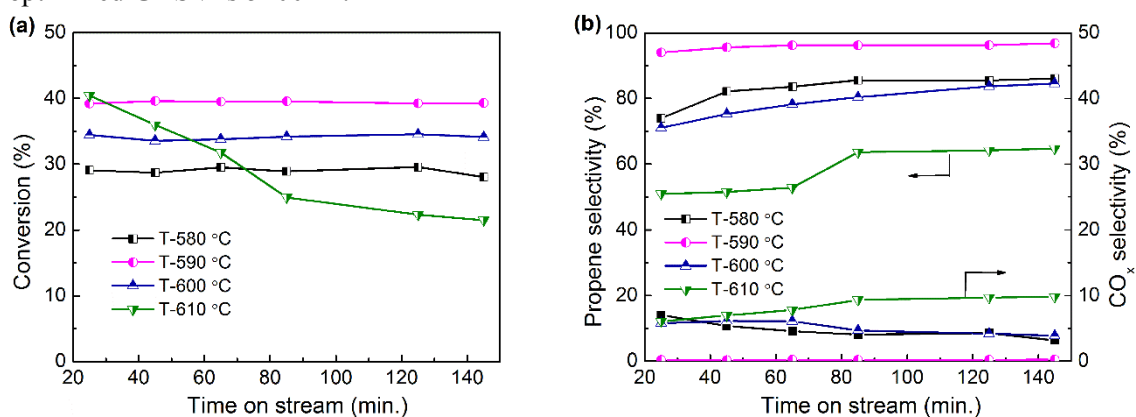
**Figure 2.** (a) Conversion vs. time on stream and (b) selectivity vs. time on stream on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with different molar ratios of air/H<sub>2</sub> in the feed for the propane dehydrogenation (Reaction conditions: total GHSV=5200 h<sup>-1</sup>, propane GHSV=1600 h<sup>-1</sup>, T=590 °C).



**Figure 3.** (a) Conversion vs. time on stream and (b) selectivity vs. time on stream on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with different GHSV for propane dehydrogenation (Reaction conditions: C<sub>3</sub>H<sub>8</sub>:air:H<sub>2</sub>=4:5:4, T=590 °C).

Figure 3 reveals the effect of GHSV on the performance of propane dehydrogenation by varying the total flow rate while keeping the feed composition at C<sub>3</sub>H<sub>8</sub>:air:H<sub>2</sub>=4:5:4 and volume of catalysts

constant. As shown in Figure 3, the propane conversion and the propene selectivity first increases and then decreases with the increase of GHSV. The catalyst shows the best dehydrogenation performance at the gas hourly space velocity of  $5200 \text{ h}^{-1}$ . Generally, the side reactions are more likely to happen due to the longer contact time between materials and catalysts in the case of lower GHSV, at which, the selectivity of  $\text{CO}_x$  also increased in the likelihood of deep oxidation of alkane. In contrast to this, the shorter contact time at  $\text{GHSV}=6500 \text{ h}^{-1}$  more favor the timely desorption of propene and thus diminishing the occurrence of side reactions, the propene selectivity is correspondingly improved thereby. Moreover, it can be noted that the propene selectivity increases with the time on stream to some extent at the lowest space velocity. This behavior may be explained by the changes of the surface morphology of catalyst in the reaction process. As reported [16], hydrogenolysis and coking reaction was more sensitive to the support structure than the dehydrogenation, any inactive species on the surface may act as a site diluent and should increase the selectivity toward dehydrogenation. Coke deposited on the support would act as an inactive species and thereby improve propene selectivity. Comprehensively, the GHSV has an obvious influence on the activity and product selectivities, and the optimized GHSV is  $5200 \text{ h}^{-1}$ .



**Figure 4.** (a) Conversion vs. time on stream and (b) selectivity vs. time on stream on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with different reaction temperature for propane dehydrogenation (Reaction conditions: total GHSV=5200 h<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>:air:H<sub>2</sub>=4:5:4).

Figure 4 demonstrates the conversions and selectivities for dehydrogenation of propane with H<sub>2</sub> and air at various reaction temperatures. It can be seen that, both the conversion and propene selectivity first increases and then decreases with the increase of reaction temperature, and achieve their maximum values at 590 °C. Since the catalytic dehydrogenation reaction is endothermic, temperature increased is favorable to the production of propene. Besides, it can be seen that the catalyst has the better stability with an almost constant conversion of propane and selectivity of propene in the cases of the reaction temperature less than 610 °C. Accordingly, it can be speculated that the cracking reaction and deep oxidation of alkane can hardly take place. When the reaction temperature continuously rose to 610 °C, however, the CO<sub>x</sub> exhibit the highest selectivity, and the conversion of propane decreases from 40.4% to 21.5% with the reaction carrying on, meaning that the side reactions and carbon deposition are more likely to happen and thus result in the drastically decreased of propene selectivity. This phenomenon indicate that reaction temperature has a great influence on the dehydrogenation performance of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. The reaction temperature should not be higher than 600 °C.

#### 4. Conclusions

The Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared through a simple impregnation-reduction method and applied in the dehydrogenation reaction of propane with air present. Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits the higher propane conversion of 39.2%-39.6% and propene selectivity of 94.0%-97.0%, simultaneously with the stable catalytic activity. The addition of suitable amount of air to feed can greatly improve the

catalytic performance of propane dehydrogenation. The steam generated by the hydrogen combustion is favorable for the dehydrogenation reaction and improve the conversion of propane and selectivity of propene. The process conditions of propane dehydrogenation, including GHSV, air/H<sub>2</sub> mole ratio and reaction temperature, were further studied. The results show that the increase of GHSV can short the contact time between raw materials and catalysts and thus increases the selectivity of propene, but decreases the conversion of propane. The appropriate space velocity is set as 5200h<sup>-1</sup>. Too-large air/H<sub>2</sub> mole ratio results in a lower selectivity of propene, while too-low ratio causes the decrease of propane conversion. The fitting air/H<sub>2</sub> mole ratio is set as 5:4. Additionally, reaction temperature greatly impacts the dehydrogenation performance: both too-high and too-low reaction temperature produce lower yield of propene, and it should be below 600 °C. Finally, it is expected that the research of this paper can offer a reference to design high-performance catalysts and improve the catalytic performance for the dehydrogenation of light alkanes.

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### References

- [1] Ertl G, Knözinger H, Schüth F and Weitkamp J 2008 *Handbook of heterogeneous catalysis* (Weinheim: Wiley-VCH)
- [2] Shen L L, Xia K, Lang W Z, Chu L F, Yan X and Guo Y J 2017 *Chem. Eng. J.* **324** 336-346
- [3] Farnaz T Z, Abbas T, Khodayar G and Saeed S 2016 *J. Nat. Gas. Sci. Eng.* **30** 156-163
- [4] Sattler J J H B, Ruiz-Martínez J, Santillan-Jimenez E and Weckhuysen B M 2014 *Chem. Rev.* **114** 10613-53
- [5] Li B, Xu Z X, Chu W, Luo S Z and Jing F L 2017 *Chinese J. Catal.* **38** 726-735
- [6] Zhou H L, Gong J J, Xu B L, Deng S C, Ding Y H and Yu L 2017 *Chinese J. Catal.* **38** 529-536
- [7] Kogan S B, Schramm H and Herskowitz M, 2001 *Appl. Catal. A-Gen.* **208** 185-191
- [8] Shan Y L, Sui Z J, Zhu Y, Chen D and Zhou X G 2015 *Chem. Eng. J.* **278** 240-248
- [9] Grasselli R K, Stern D L and Tsikoyiannis J G, 1999 *Appl. Catal. A-Gen.* **189** 1-8
- [10] John G T, David L S and Robert K G 1999 *J. Catal.* **184** 77-86
- [11] Kaneko S, Arakawa T, Ohshima M, Kurokawa H and Miura H 2009 *Appl. Catal. A-Gen.* **356** 80-87
- [12] Robert K G, David L S and John G T 1999 *Appl. Catal. A-Gen.* **189** 9-14
- [13] Graaf E A, Zwanenburg G, Rothenberg G and Blik A 2005 *Org. Process Res. Dev.* **9** 397-403
- [14] Kuznetsova N I et al. 2014 *Appl. Catal. A-Gen.* **477** 1-7
- [15] Kuznetsova N I, Popova G Y, Kuznetsova L I, Zaikovskii V I, Koscheev S V, Andrushkevich T V, Lisitsyn A S, Likholobov V A and Han S 2015 *Catal. Today* **245** 179-185
- [16] Fattahi M, Khorasheh F, Sahebdehfar S, Zangeneh F T, Ganji K and Saeedizad M 2011 *Scientia Iranica* **18** 1377-83
- [17] Ma Z H, Mo Y J, Li J, An C H and Liu X N 2015 *J. Nat. Gas. Sci. Eng.* **27** 1035-42
- [18] Liu C 2010 *Study of the explosion limits of C<sub>3</sub>/H<sub>2</sub>/O<sub>2</sub> mixture* (Master degree thesis, Shanghai: East China University of Science and Technology)
- [19] Kotanjac Z 2009 *Development of packed bed membrane reactor for the oxidative dehydrogenation of propane* (PhD dissertation, Enschede: University of Twente)
- [20] Biloen P, Dautzenberg F M and Sachtler W M H 1977 *J. Catal.* **50** 77-86
- [21] Li Q, Sui Z J, Zhou X G and Chen D 2011 *Appl. Catal. A-Gen.* **398** 18-26