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One-Step Fabrication of PtSn/γ-Al_2O_3 Catalysts with La Post-Modification for Propane Dehydrogenation

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Abstract: The catalytic dehydrogenation of propane to propene is an alternative technique to supplement the traditional steam cracking and catalytic cracking process for satisfying the continuously increasing demand for propylene downstream products. In this study, the parent PtSn/γ-Al_2O_3 catalyst was fabricated via the one-step method for the subsequent La post-modification to prepare the catalysts for propane dehydrogenation. The prepared and spent catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, scanning electron microscope (SEM), NH_3 temperature-programmed desorption (NH_3-TPD), H_2 temperature-programmed desorption (H_2-TPR), and thermogravimetric (TG) analysis. The catalytic performance and characterization results demonstrated that the addition of La into the parent catalyst could significantly improve the catalytic performance of the prepared catalyst. Especially, the PtSn-La2.2 catalyst with the 2.2 wt.% La addition exhibited the stable and highest propylene selectivity (>84%) under the investigation time of 800 min. The introduced La exhibits the ability to adjust the textural properties of the obtained catalysts, curb the acidity of support, promote the reduction of Pt species, and reduce the carbon accumulation on the prepared catalysts.

Keywords: propane dehydrogenation; lanthanum; PtSn catalysts; propylene

1. Introduction

Propylene, as one of the most important types of compounds in the modern petrochemical industry, is mainly used to produce polypropylene, acrylonitrile, propylene oxide, and other important intermediates [1–7]. Propylene is traditionally supplied from the steam cracking and the catalytic cracking process of naphtha or other oil byproducts [8]. In recent years, the domestic and international market demand for propylene is dramatically growing with the continuous exploitation of propylene downstream products. There is an ever-growing gap between the demand for propylene and the productivity of traditional processes. Therefore, some on-purpose propylene production technologies (e.g., methanol to olefins, methanol to propylene, propane dehydrogenation, etc.) are widely developed to satisfy the increasing demand for propylene. Among these technologies, the propane dehydrogenation (PDH), regarded as a potential and high value-added propylene production route, has gained much attention [9,10]. This process is an endothermic and thermodynamically equilibrium-limited reaction [3,11], which needs the operating conditions of high-temperature and low-pressure for realizing the high propylene yield. The high reaction temperature of 550–700 °C could lead to fast catalyst deactivation as well as unwanted side reactions, such as isomerization, hydrogenolysis, and dehydrocyclization [12,13]. Presently, the platinum-based catalysts (UOP Oleflex process) and chromium oxide-based catalysts (Lummus Catofin process) were mainly employed in the commercial PDH processes [14]. However, the preparation and application of chromium oxide-based catalysts would be limited due to the environmental pollution issues.

Platinum-based catalysts with excellent performance to activate the C–H bonds of alkanes exhibit high activity in catalytic dehydrogenation of low-carbon alkanes [15,16]. The relatively low selectivity for desired olefin products is one of the drawbacks of utilizing the platinum-based catalysts. Furthermore, fast deactivation of these catalysts due to the carbon accumulation and the Pt sintering is still a major problem [17–19]. Many studies had attempted to modify the catalytic properties of platinum-based catalysts by the addition of promoters (Co, Sn, Cu, Fe, Ga, Ge, etc.) [20–25]. The effect of those promoters on active metals can be summarized as the geometric and electronic effect, which could improve activity, selectivity, and stability of Pt-based catalysts. Besides, some additives could also adjust the properties of supports (acidity, thermal stability, surface structure, etc.) to create a suitable catalytic environment of PDH reaction. Especially for Sn additives, the existence of Sn not only could reduce the size of Pt particles, which suppresses side reactions occurring on the larger Pt ensembles (geometric effect), but also change the electronic properties of Pt by transferring electrons to Pt atoms, thus changing adsorption performance of active metals (electronic effect) [16,26,27]. Besides, Sn could facilitate the removal of carbon precursors from metal sites to the support, thus prolonging the catalyst lifetime [28].

In addition, alkali, alkali earth, and rare earth metals were also added to improve the catalyst selectivity and stability [1,16]. K and Li could curb the strong acidity of the catalyst support to realize the high activity and stability of the PtSn catalyst [29]. Doping γ-Al_2O_3 with alkali (IA) and alkali earth (IIA) metals can not only adjust the acid properties, but also modify the interaction between the PtSn active components and the support [30]. The addition of Ce into the PtSn catalysts could stabilize the active states of Pt, Sn, and support, and suppress the carbon deposition, thus improving the catalytic performance for PDH [31]. Similar to Ce, the addition of La into the PtSn catalysts could not only improve catalytic performance in the respect of anti-coking, but also improve the interaction between Pt and SnOx species by maintaining the oxidation state of Sn, which is favorable for increasing activity [32,33]. Therefore, the selection and introduction of proper promoters into the platinum-based catalysts is crucial for enhancing their catalytic performance in PDH reaction.

In this work, the parent PtSn/γ-Al_2O_3 catalyst was prepared by the one-pot method, the Pt and Sn species were homogeneously dispersed in the pseudo-boehmite gel, leading to the high dispersion of the metal on the obtained PtSn/Al_2O_3 catalyst after the calcination. Then, the parent catalyst was post-modified by the La addition to fabricate catalysts for PDH reaction. The obtained catalysts were intensively characterized and tested the catalytic performance. The effects of La were investigated in detail to clarify the structure–activity relationship between the catalyst physicochemical properties and the catalytic performance in the PDH reaction.

2. Results

2.1. Crystalline Analysis

The crystalline phase of parent and La-modified catalysts is characterized by X-ray powder diffraction, as shown in Figure 1. All samples exhibit four typical characteristic peaks of γ-Al_2O_3 phase (PDF#10-0425) at ~37.8°, ~39.5°, ~45.5°, and ~66.7°, respectively, which indicates that the crystalline phase of γ-Al_2O_3 support is maintained after the impregnation of metal species. Moreover, the diffraction peaks corresponding to Pt, Sn, and La are not detected by XRD because of the extremely low loading amounts and/or the high dispersion of them in the parent and PtSn-LaX catalysts.

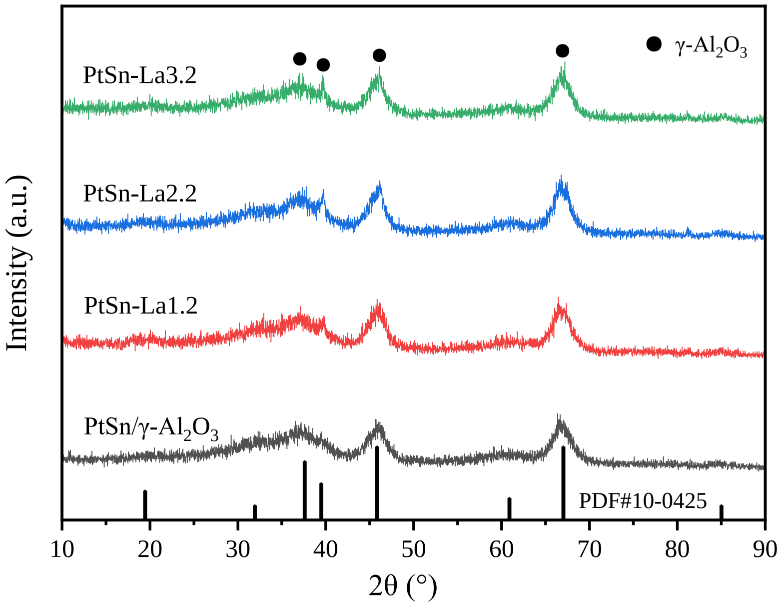

Figure 1. XRD patterns of the parent PtSn/γ-Al_2O_3 catalyst and PtSn-LaX catalysts.

2.2. Textural Properties of Catalysts

The textural properties of parent PtSn/γ-Al_2O_3 and corresponding PtSn-LaX catalysts were characterized by the technique of low-temperature nitrogen adsorption–desorption, as depicted in Figure 2. The nitrogen adsorption–desorption isotherms of all catalysts can be classified into the typical type-IV with a hysteresis loop according to the IUPAC category, suggesting the existence of the mesoporous structures of γ-Al_2O_3. Moreover, it can be seen from Table 1 that the parent PtSn/γ-Al_2O_3 catalyst with board pore size distribution possesses the largest specific surface area and pore volume. After the introduction of La, the PtSn-LaX catalysts experience a negligible reduction of specific surface area and pore volume due to the partial blockage of the pore channels during the wetness impregnation of La species and/or the collapse of some brittle pores during the second calcination process, of which phenomenon was also found in the previous studies [34]. However, the severe loss of the mesopore occurs when the addition amount of La is up to 3.2 wt.% (Figure 2b). Therefore, the appropriate addition amount of La (2.2 wt.%) is beneficial to adjust the textural properties of the PtSn-La2.2, as reflected in superior catalytic PDH performance (Figure 6). Furthermore, the morphology changes before and after La post-modification were investigated by the SEM, as shown in Figure 3. It can be observed that the parent PtSn/γ-Al_2O_3 and corresponding PtSn-LaX catalysts exhibit a similar microstructure to the catalyst particles, which are formed by the aggregation of the primary clusters. This implies that La post-modification has a slight effect on the basic morphologies of parent catalyst, which is consistent with the results of the textural properties of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts in Table 1.

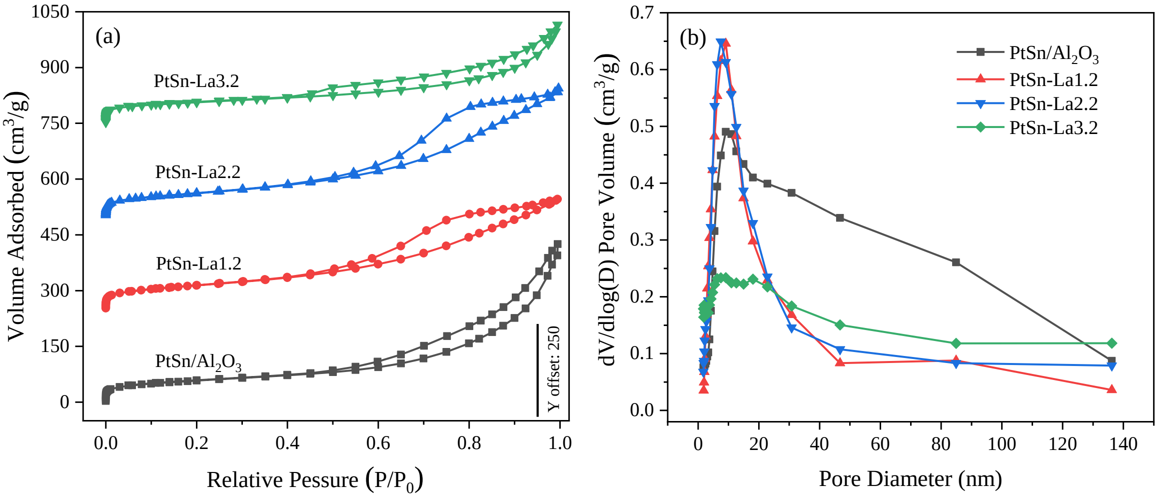

Figure 2. Low-temperature N_2 adsorption–desorption isotherms (**a**) and the corresponding pore size distributions (**b**) of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts.

Table 1. Textural properties of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	D_{ave} (nm)	Loadings (wt.%)		
				Pt	Sn	La
PtSn/γ-Al_2O_3	229	0.553	9.32	0.6	0.1	-
PtSn-La1.2	208	0.542	9.17	0.6	0.1	1.2
PtSn-La2.2	215	0.545	9.25	0.6	0.1	2.2
PtSn-La3.2	199	0.512	9.11	0.6	0.1	3.2

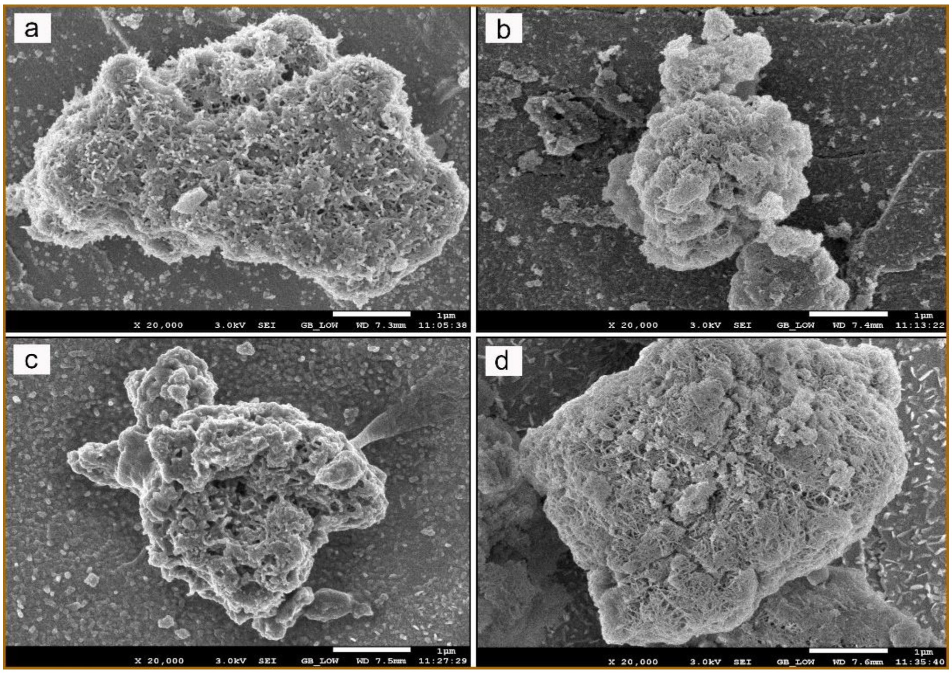

Figure 3. SEM images of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts. (**a**) PtSn/γ-Al_2O_3; (**b**) PtSn-La1.2; (**c**) PtSn-La2.2; (**d**) PtSn-La3.2.

2.3. The Evaluation of Reduction Behavior

Figure 4 shows the H_2-TPR profiles of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts to investigate the reduction properties. The main peak of the hydrogen consumption for all catalysts is located at the temperature of <200 °C, which is ascribed to the reduction of Pt species. Moreover, this peak of

PtSn-LaX catalysts shifts slightly to the low temperature after La post-modification, illustrating that the existence of La can promote the reduction of Pt species for improving the dispersion of Pt. It had been reported that the electron-pushing effect of La could increase the electron density of Pt atoms, which is beneficial to the reduction of Pt species [35]. Furthermore, there is no significant change in the temperature range of 200 to 700 °C, which could be attributed to the inhibition effect of La to the reduction of SnOx species [32]. Moreover, the temperature of 500 °C used in the reduction process was sufficient to obtain the reduced catalysts for the subsequent PDH reaction.

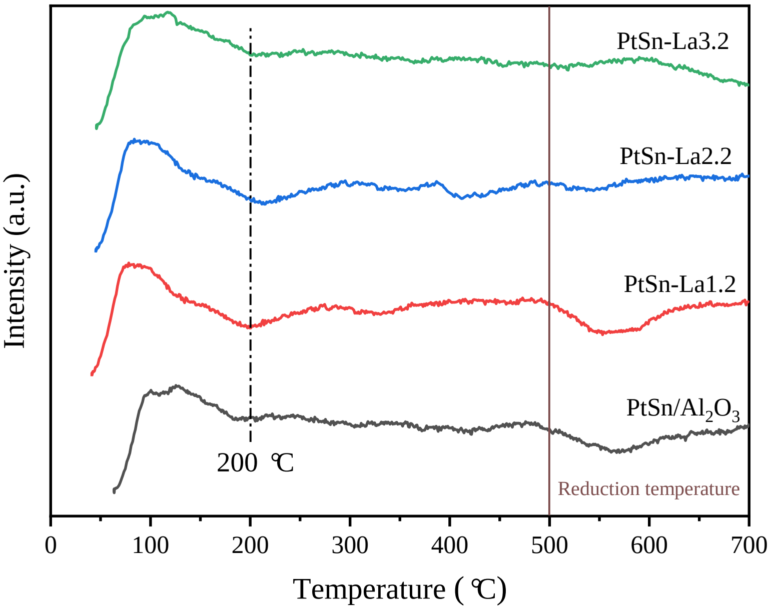

Figure 4. The H_2-TPR profiles of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts.

2.4. Acidity Analysis

The acidity properties of the parent PtSn/γ-Al_2O_3 and PtSn-LaX catalysts were evaluated by NH_3-TPD, and the corresponding profiles are demonstrated in Figure 5. There are two peaks for all catalysts in the temperature range of 50 to 300 °C (I) and >300 °C (II), which could be attributed to the desorption of NH_3 molecules from weak and strong acidity sites of catalysts, respectively. The amount of acid sites of the prepared catalysts decreases with the elevated content of La (up to 2.2 wt.%). Furthermore, the acid intensities of the weak acid center become weaker progressively because the desorption temperature of the ammonia shifts to the lower temperature. However, with the continuous addition of La (3.2 wt.%), the excessive addition of La can lead to an increase in catalyst acidity, which could be the reason for the deterioration of PDH performance over the PtSn-La3.2 catalyst, as discussed in the following section. Generally, the Al_2O_3 with excellent properties, such as the large specific surface, high stability, and high mechanical strength, is widely employed as the support in Pt-based catalysts [14]. However, the acidity of most Al_2O_3 is relatively strong and inappropriate for Pt-based catalysts in PDH, as evidenced by the performance evaluation result of PtSn/γ-Al_2O_3 catalysts in Figure 6. The addition of La into the parent catalyst can weaken or curb the acidity of support and suppress the unwanted side reactions that occurred on those sites, thus leading to the high propene selectivity over the La-modified catalysts in the PDH process.

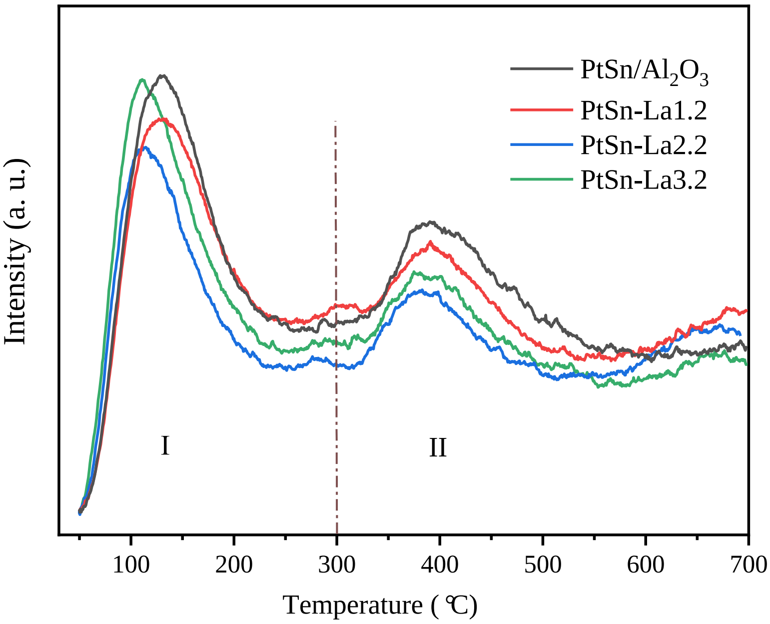

Figure 5. The NH_3-TPD profiles of the prepared catalysts.

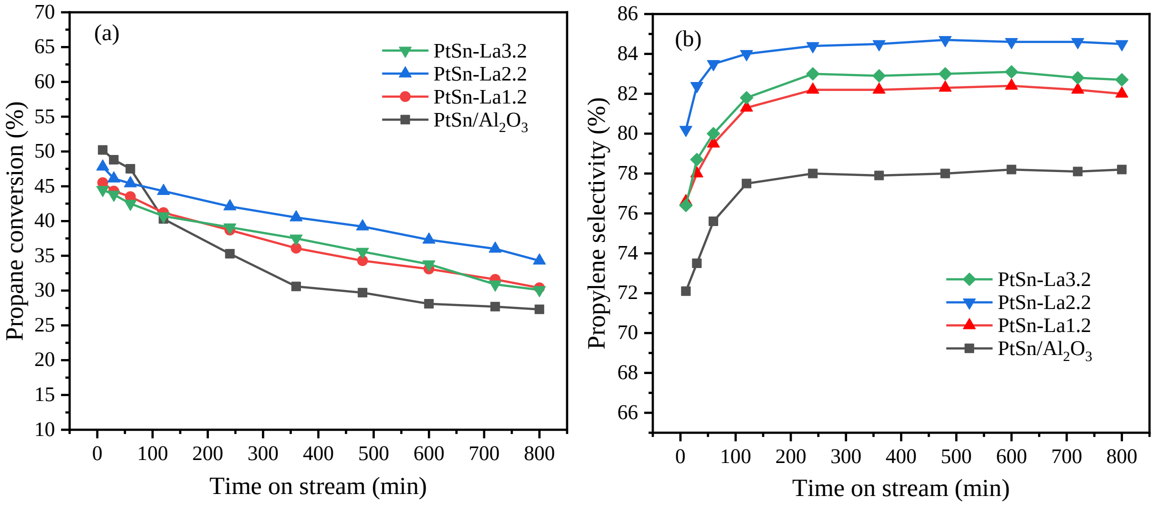

Figure 6. Catalytic performance of the parent PtSn/γ-Al_2O_3 catalyst and PtSn-LaX catalysts in PDH reaction. (**a**) Propane conversions with time on stream. (**b**) Propylene selectivities with time on stream.

2.5. Propane Dehydrogenation Performance

The catalytic performance of obtained catalysts in the PDH process with time on stream is shown in Figure 6. Compared to the PtSn-LaX catalysts, the parent PtSn/γ-Al_2O_3 catalyst shows relatively low propane conversion and rapid deactivation due to the accumulated carbon on the Pt active sites (Figure 6a), which is the common phenomenon in the Pt-based catalyst [35]. The propane conversion of parent PtSn/γ-Al_2O_3 catalyst is 50.2% initially and then reduces rapidly to 27.2% after 800 min reaction. In contrast, the catalytic activity and stability of the PtSn-LaX catalysts are significantly enhanced after the addition of La into the parent PtSn/γ-Al_2O_3 catalyst. The PtSn-La2.2 catalyst with the 2.2 wt.% La addition exhibits the superior catalytic performance of PDH with the propane conversion rate of >34% under the investigation time, indicating that the addition of La could remarkably influence the catalytic propane dehydrogenation performances of the prepared catalysts. The results of propene selectivities over PtSn-LaX catalysts in Figure 6b indicate that there is an ascending process of propylene selectivities over these catalysts within 2 h, followed by the relatively stable stage for each catalyst. With the increase of La content in the prepared PtSn-LaX catalysts, the selectivity to propene has also improved.

Correspondingly, the maximum propylene selectivity (>84%) is obtained over the PtSn-La2.2 catalyst. However, the propylene selectivity starts to deteriorate over the PtSn-La3.2 catalyst with the excessive addition (3.2 wt.%) of La. Therefore, the appropriate addition amount (2.2 wt.%) of La can enhance the anti-coking ability for prolonging the catalyst lifetime with the relatively high propane conversion and propylene selectivity over the PtSn-La2.2 catalyst during the PDH process.

To better understand the catalytic performance of prepared PtSn-LaX catalysts, the activity comparison results over the Pt-based catalysts are listed in Table 2. The PtSn-La2.2, PtSnNa/1.0La-Al, and PtSnNaLa(1.4%)/ZSM-5 catalysts exhibit higher stability than Pt–Sn/La(10%)-Al catalyst under the investigation time. Although the propylene selectivity over the PtSn-La2.2 catalyst is relatively lower than that of the other catalysts, the lifetime of the PtSn-La2.2 catalyst was prolonged to 800 min. Moreover, the one-step method employed in this study is an easy way to fabricate PtSn-LaX catalysts for the combination of support preparation and impregnation of active components.

Table 2. Comparison of catalytic performance between PtSn-LaX and other related catalysts.

Catalysts	T/°C	X1 [1]	X2 [2]	Reaction Time	Selectivity	References
PtSn-La2.2	600	47.8	34.3	800 min	84.6	This work
PtSnNa/1.0La-Al	590	41.1	35.9	360 min	96.2	[32]
PtSnNaLa(1.4%)/ZSM-5	590	~41.6	37.2	300 min	~97.5	[35]
Pt–Sn/La(10%)-Al	600	~52	~25	180 min	~97	[36]

[1] X1 represents the initial propane conversion; [2] X2 represents the final propane conversion.

2.6. The Evaluation of Carbon Deposition over the Spent Catalysts

The TG technique was employed to investigate the degree of carbon deposition over the spent catalysts after the PDH reactions, as depicted in Figure 7. It can be seen that the weight loss of spent catalysts occurs as the temperature rises from 30 °C to 800 °C. The weight loss process can be divided into two stages (I and II). The weight loss at stage I of <300 °C is due to the removal of the volatile organic components in the spent catalysts, and the burning of deposited carbon on the catalyst takes place at stage II of 300–500 °C with maximum weight loss. The parent PtSn/γ-Al_2O_3 catalyst suffers severe carbon deposition during the PDH reaction, which is consistent with the fast decline of propane conversion in Figure 6a. However, the degree of carbon deposition could be improved after the La post-modification of the parent catalyst, especially for the PtSn-La2.2 catalyst. The carbon accumulation, which mainly results from side reactions such as isomerization, hydrogenolysis, and dehydrocyclization, could cover active metals and lead to the fast decrease in activity [37]. The improvement in stability and selectivity of the La-modified PtSn/γ-Al_2O_3 catalyst can be attributed to the inhibiting effect of La on side reactions. These results reveal that the addition of La can significantly reduce the carbon deposition on the prepared catalysts, thus prolong the catalyst lifetime.

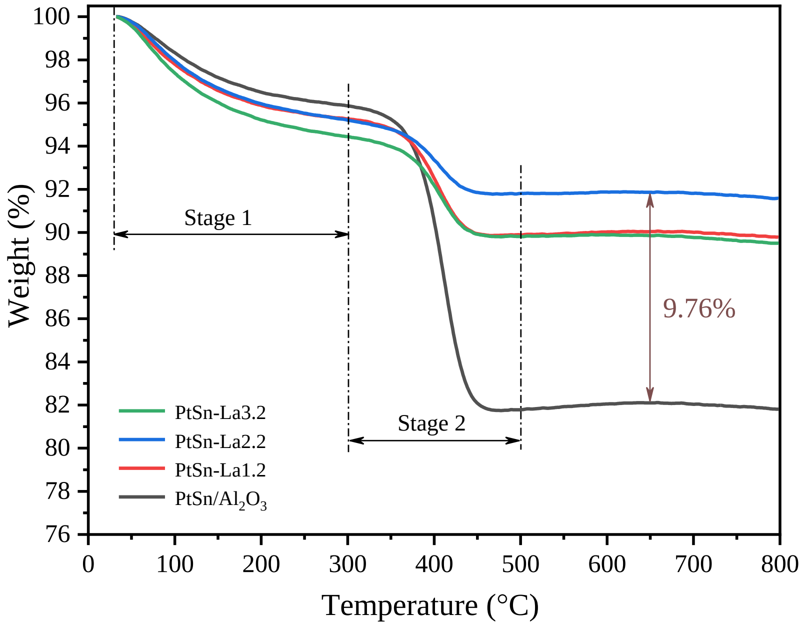

Figure 7. The thermogravimetric (TG) curves of the spent catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

The parent PtSn/γ-Al_2O_3 catalysts were prepared by the one-step method [38]. The pseudo-boehmite, $H_2PtCl_6{\cdot}6H_2O$, $SnCl_2{\cdot}2H_2O$, and $La(NO_3)_3{\cdot}6H_2O$ were used as the raw materials. The pseudo-boehmite was purchased from Yantai Henghui Chemical Co. Ltd., Yantai, China, and others were supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. First, the preweighted pseudo-boehmite was dispersed in deionized water under continuous stirring at 60 °C. Then, the $H_2PtCl_6{\cdot}6H_2O$ and $SnCl_2{\cdot}2H_2O$ were added into the above mixture. After constant stirring for 60 min, the diluted ammonia was employed to adjust the solution pH value to 7, followed by stirring until the pseudo-boehmite gel was formed. The obtained gel was aged at room temperature for 24 h, then dried at 100 °C overnight and calcined at 600 °C for 4 h. The parent PtSn/γ-Al_2O_3 catalyst (40–60 mesh) was obtained after pressing, grinding, and sieving for the subsequent PDH reaction. The loading amount of Pt and Sn in all catalysts is 0.6 wt.% and 0.1 wt.%, respectively.

For the fabrication of the La-modified PtSn/γ-Al_2O_3 catalysts, the preweighted $La(NO_3)_3{\cdot}6H_2O$ was introduced into the parent PtSn/γ-Al_2O_3 catalyst by the incipient wetness impregnation method. Typically, $La(NO_3)_3{\cdot}6H_2O$ was dissolved in an appropriate amount of deionized water and impregnated on parent PtSn/γ-Al_2O_3 catalyst. Then, the catalyst precursor was dried at 100 °C overnight, then calcined at 600 °C for 4 h. The obtained La-modified PtSn/γ-Al_2O_3 catalysts were denoted as PtSn-LaX, where X was the mass ratio of La to the catalyst (X = 0, 1.2, 2.2, 3.2 wt.%, respectively).

3.2. Characterization

The XRD patterns of prepared PtSn-LaX catalysts were recorded on a D-MAX 2500/PC diffractometer equipped with Cu-Kα radiation (40 kV, 40 mA) in the 2θ range of 10° to 90°. The low-temperature N_2 adsorption–desorption tests were conducted on the instrument of ASAP2020 PLUS HD88 (Micrometritics, Norcross, GA, USA) to determine the surface area and the pore size distribution of the prepared catalysts. SEM characterization was performed with a scanning electron microscope (JSM-7500F, JEOL, Tokyo, Japan) operating at 3.0 kV. The acidic properties of samples were evaluated by NH_3-TPD on Micromeritics AutoChem II 2920 apparatus (Micrometritics, Norcross, GA, USA). The H_2-TPR experiments were carried out to investigate the reducibility of the samples on the ASAP 2010C apparatus (Micrometritics, Norcross, GA, USA). TG analysis was carried out on the STA449

C/3/F thermal analyzer (NETZSCH, Selb, Germany) to evaluate the degree of carbon deposition on the spent catalysts.

3.3. Activity Evaluation of Catalysts

The continuous stainless-steel fixed-bed reactor (I.D.: 18 mm) (Beiyang Chemical Engineering Experimental Equipment Co., Ltd., Tianjin, China) was used to evaluate the catalytic propane dehydrogenation performance over the prepared PtSn-LaX catalysts under atmospheric pressure. Before the reaction, 5.0 g of catalyst (40–60 mesh) was first loaded into the reactor, then in situ reduced under the gas mixture of 10 vol% H_2/N_2 (160 mL/min) at 500 °C for 10 h. After the reduction process, the propane (80 mL/min) was switched for the PDH reaction at the temperature of 600 °C. The on-line gas chromatograph (GC-6890A, Lunan Ruihong Chemical Instrument Co., Ltd, Tengzhou, Shandong, China) was employed to analyze the products for calculating the propane conversion and propylene selectivity.

4. Conclusions

The parent PtSn/γ-Al_2O_3 catalyst was successfully prepared by the one-step method for the subsequent La post-modification to fabricate the PtSn-LaX catalysts with different content of La. The results of the activity evaluation of the PDH reaction revealed that La post-modification is an effective way to improve catalytic performance. The PtSn-La2.2 catalyst with the 2.2 wt.% of La exhibits the highest propane conversion (>34%) and propylene selectivity (>84%) under the investigation time. The characterization results indicate that La post-modification has a slight effect on the basic morphologies as well as the textural properties of the obtained catalysts. Moreover, the appropriate addition amount of La into the parent catalyst by the post-modification method can adjust the textural properties of the PtSn-LaX catalysts, curb the acidity of support to suppress the unwanted side reactions, promote the reduction of Pt species for improving the dispersion of Pt, and significantly reduce the carbon deposition on the prepared catalysts. The results obtained in this study suggest that the structure–activity relationship can be elucidated after further investigation of the effects of the promoters on the prepared catalysts during the PDH reaction.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jang, E.J.; Lee, J.; Jeong, H.Y.; Kwak, J.H. Controlling the acid-base properties of alumina for stable PtSn-based propane dehydrogenation catalysts. *Appl. Catal. A Gen.* **2019**, *572*, 1–8. [CrossRef]
2. Liu, J.; Li, J.; Rong, J.; Liu, C.; Dai, Z.; Bao, J.; Da, Z.; Zheng, H. Defect-driven unique stability of Pt/carbon nanotubes for propane dehydrogenation. *Appl. Surf. Sci.* **2019**, *464*, 146–152. [CrossRef]
3. Saerens, S.; Sabbe, M.K.; Galvita, V.V.; Redekop, E.A.; Reyniers, M.-F.; Marin, G.B. The Positive Role of Hydrogen on the Dehydrogenation of Propane on Pt(111). *ACS Catal.* **2017**, *7*, 7495–7508. [CrossRef]
4. Li, Q.; Yang, G.; Wang, K.; Wang, X. Preparation of carbon-doped alumina beads and their application as the supports of Pt–Sn–K catalysts for the dehydrogenation of propane. *React. Kinet. Mech. Catal.* **2020**, *129*, 805–817. [CrossRef]
5. Dai, Y.; Gu, J.; Tian, S.; Wu, Y.; Chen, J.; Li, F.; Du, Y.; Peng, L.; Ding, W.; Yang, Y. γ-Al_2O_3 sheet-stabilized isolate Co^{2+} for catalytic propane dehydrogenation. *J. Catal.* **2020**, *381*, 482–492. [CrossRef]

6. Shan, Y.-L.; Wang, T.; Sui, Z.-J.; Zhu, Y.-A.; Zhou, X.-G. Hierarchical $MgAl_2O_4$ supported Pt-Sn as a highly thermostable catalyst for propane dehydrogenation. *Catal. Commun.* **2016**, *84*, 85–88. [CrossRef]
7. Liu, G.; Zhao, Z.-J.; Wu, T.; Zeng, L.; Gong, J. Nature of the Active Sites of VO_x/Al_2O_3 Catalysts for Propane Dehydrogenation. *ACS Catal.* **2016**, *6*, 5207–5214. [CrossRef]
8. Zhu, J.; Yang, M.-L.; Yu, Y.; Zhu, Y.-A.; Sui, Z.-J.; Zhou, X.-G.; Holmen, A.; Chen, D. Size-Dependent Reaction Mechanism and Kinetics for Propane Dehydrogenation over Pt Catalysts. *ACS Catal.* **2015**, *5*, 6310–6319. [CrossRef]
9. Jiang, F.; Zeng, L.; Li, S.; Liu, G.; Wang, S.; Gong, J. Propane Dehydrogenation over Pt/TiO_2-Al_2O_3 Catalysts. *ACS Catal.* **2015**, *5*, 438–447. [CrossRef]
10. Li, J.; Li, J.; Zhao, Z.; Fan, X.; Liu, J.; Wei, Y.; Duan, A.; Xie, Z.; Liu, Q. Size effect of TS-1 supports on the catalytic performance of PtSn/TS-1 catalysts for propane dehydrogenation. *J. Catal.* **2017**, *352*, 361–370. [CrossRef]
11. Zangeneh, F.T.; Taeb, A.; Gholivand, K.; Sahebdelfar, S. The effect of mixed HCl–KCl competitive adsorbate on Pt adsorption and catalytic properties of Pt–Sn/Al_2O_3 catalysts in propane dehydrogenation. *Appl. Surf. Sci.* **2015**, *357*, 172–178. [CrossRef]
12. Wang, H.-Z.; Zhang, W.; Jiang, J.-W.; Sui, Z.-J.; Zhu, Y.-A.; Ye, G.-H.; Chen, D.; Zhou, X.-G.; Yuan, W.-K. The role of H_2S addition on Pt/Al_2O_3 catalyzed propane dehydrogenation: A mechanistic study. *Catal. Sci. Technol.* **2019**, *9*, 867–876. [CrossRef]
13. Vu, B.K.; Song, M.B.; Ahn, I.Y.; Suh, Y.-W.; Suh, D.J.; Kim, J.S.; Shin, E.W. Location and structure of coke generated over Pt–Sn/Al_2O_3 in propane dehydrogenation. *J. Ind. Eng. Chem.* **2011**, *17*, 71–76. [CrossRef]
14. Jung, J.-W.; Kim, W.-I.; Kim, J.-R.; Oh, K.; Koh, H.L. Effect of Direct Reduction Treatment on Pt–Sn/Al_2O_3 Catalyst for Propane Dehydrogenation. *Catalysts* **2019**, *9*, 446. [CrossRef]
15. Shi, L.; Deng, G.-M.; Li, W.-C.; Miao, S.; Wang, Q.-N.; Zhang, W.-P.; Lu, A.-H. Al_2O_3 Nanosheets Rich in Pentacoordinate Al^{3+} Ions Stabilize Pt-Sn Clusters for Propane Dehydrogenation. *Angew. Chem. Int. Ed.* **2015**, *54*, 13994–13998. [CrossRef] [PubMed]
16. Sattler, J.J.H.B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114*, 10613–10653. [CrossRef] [PubMed]
17. Wang, H.; Sun, L.; Sui, Z.J.; Zhu, Y.; Ye, G.; Chen, D.; Zhou, X.; Yuan, W. Coke Formation on Pt–Sn/Al_2O_3 Catalyst for Propane Dehydrogenation. *Ind. Eng. Chem. Res.* **2018**, *57*, 8647–8654. [CrossRef]
18. Wang, G.; Zhu, X.; Li, C. Recent Progress in Commercial and Novel Catalysts for Catalytic Dehydrogenation of Light Alkanes. *Chem. Rec.* **2020**, *20*, 604–616. [CrossRef]
19. Fan, X.; Liu, D.; Sun, X.; Yu, X.; Li, D.; Yang, Y.; Liu, H.; Diao, J.; Xie, Z.; Kong, L.; et al. Mn-doping induced changes in Pt dispersion and Pt_xMn_y alloying extent on Pt/Mn-DMSN catalyst with enhanced propane dehydrogenation stability. *J. Catal.* **2020**, *389*, 450–460. [CrossRef]
20. Cesar, L.G.; Yang, C.; Lu, Z.; Ren, Y.; Zhang, G.; Miller, J.T. Identification of a Pt_3Co Surface Intermetallic Alloy in Pt–Co Propane Dehydrogenation Catalysts. *ACS Catal.* **2019**, *9*, 5231–5244. [CrossRef]
21. Ren, G.-Q.; Pei, G.-X.; Ren, Y.-J.; Liu, K.-P.; Chen, Z.-Q.; Yang, J.-Y.; Su, Y.; Liu, X.-Y.; Li, W.-Z.; Zhang, T. Effect of group IB metals on the dehydrogenation of propane to propylene over anti-sintering $Pt/MgAl_2O_4$. *J. Catal.* **2018**, *366*, 115–126. [CrossRef]
22. Kobayashi, S.; Kaneko, S.; Ohshima, M.-A.; Kurokawa, H.; Miura, H. Effect of iron oxide on isobutane dehydrogenation over Pt/Fe_2O_3-Al_2O_3 catalyst. *Appl. Catal. A Gen.* **2012**, *417–418*, 306–312. [CrossRef]
23. Wang, T.; Jiang, F.; Liu, G.; Zeng, L.; Zhao, Z.-j.; Gong, J. Effects of Ga doping on Pt/CeO_2-Al_2O_3 catalysts for propane dehydrogenation. *AIChE J.* **2016**, *62*, 4365–4376. [CrossRef]
24. Rimaz, S.; Chen, L.; Kawi, S.; Borgna, A. Promoting effect of Ge on Pt-based catalysts for dehydrogenation of propane to propylene. *Appl. Catal. A Gen.* **2019**, *588*, 117266. [CrossRef]
25. Nykänen, L.; Honkala, K. Selectivity in Propene Dehydrogenation on Pt and Pt_3Sn Surfaces from First Principles. *ACS Catal.* **2013**, *3*, 3026–3030. [CrossRef]
26. Wu, J.; Peng, Z.; Bell, A.T. Effects of composition and metal particle size on ethane dehydrogenation over $PtxSn_{100-x}/Mg(Al)O$ ($70 \leqslant x \leqslant 100$). *J. Catal.* **2014**, *311*, 161–168. [CrossRef]
27. Zhang, Y.; Zhou, Y.; Wan, L.; Xue, M.; Duan, Y.; Liu, X. Effect of magnesium addition on catalytic performance of $PtSnK/\gamma$-Al_2O_3 catalyst for isobutane dehydrogenation. *Fuel Process. Technol.* **2011**, *92*, 1632–1638. [CrossRef]

28. Zhao, S.; Xu, B.; Yu, L.; Fan, Y. Catalytic dehydrogenation of propane to propylene over highly active PtSnNa/γ-Al_2O_3 catalyst. *Chin. Chem. Lett.* **2018**, *29*, 475–478. [CrossRef]
29. Tasbihi, M.; Feyzi, F.; Amlashi, M.A.; Abdullah, A.Z.; Mohamed, A.R. Effect of the addition of potassium and lithium in Pt–Sn/Al_2O_3 catalysts for the dehydrogenation of isobutane. *Fuel Process. Technol.* **2007**, *88*, 883–889. [CrossRef]
30. De Graaf, E.A.; Rothenberg, G.; Kooyman, P.J.; Andreini, A.; Bliek, A. $Pt_{0.02}Sn_{0.003}Mg_{0.06}$ on γ-alumina: A stable catalyst for oxidative dehydrogenation of ethane. *Appl. Catal. A Gen.* **2005**, *278*, 187–194. [CrossRef]
31. Naseri, M.; Tahriri Zangeneh, F.; Taeb, A. The effect of Ce, Zn and Co on Pt-based catalysts in propane dehydrogenation. *React. Kinet. Mech. Catal.* **2018**, *126*, 477–495. [CrossRef]
32. Zhang, Y.; Zhou, Y.; Shi, J.; Zhou, S.; Zhang, Z.; Zhang, S.; Guo, M. Propane dehydrogenation over PtSnNa/La-doped Al_2O_3 catalyst: Effect of La content. *Fuel Process. Technol.* **2013**, *111*, 94–104. [CrossRef]
33. Del Angel, G.; Bonilla, A.; Peña, Y.; Navarrete, J.; Fierro, J.L.G.; Acosta, D.R. Effect of lanthanum on the catalytic properties of PtSn/γ-Al_2O_3 bimetallic catalysts prepared by successive impregnation and controlled surface reaction. *J. Catal.* **2003**, *219*, 63–73. [CrossRef]
34. Dong, A.-H.; Wang, K.; Zhu, S.-Z.; Yang, G.-B.; Wang, X.-T. Facile preparation of PtSn-La/Al_2O_3 catalyst with large pore size and its improved catalytic performance for isobutane dehydrogenation. *Fuel Process. Technol.* **2017**, *158*, 218–225. [CrossRef]
35. Zhang, Y.; Zhou, Y.; Liu, H.; Wang, Y.; Xu, Y.; Wu, P. Effect of La addition on catalytic performance of PtSnNa/ZSM-5 catalyst for propane dehydrogenation. *Appl. Catal. A Gen.* **2007**, *333*, 202–210. [CrossRef]
36. Vu, B.K.; Song, M.B.; Ahn, I.Y.; Suh, Y.-W.; Suh, D.J.; Kim, W.-I.; Koh, H.-L.; Choi, Y.G.; Shin, E.W. Propane dehydrogenation over Pt–Sn/Rare-earth-doped Al_2O_3: Influence of La, Ce, or Y on the formation and stability of Pt–Sn alloys. *Catal. Today* **2011**, *164*, 214–220. [CrossRef]
37. Li, Q.; Sui, Z.; Zhou, X.; Zhu, Y.; Zhou, J.; Chen, D. Coke Formation on Pt–Sn/Al_2O_3 Catalyst in Propane Dehydrogenation: Coke Characterization and Kinetic Study. *Top. Catal.* **2011**, *54*, 888–896. [CrossRef]
38. Natarajan, P.; Khan, H.A.; Yoon, S.; Jung, K.-D. One-pot synthesis of Pt–Sn bimetallic mesoporous alumina catalysts with worm-like pore structure for n-butane dehydrogenation. *J. Ind. Eng. Chem.* **2018**, *63*, 380–390. [CrossRef]