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Roles of Niobium on the Dehydrogenation of Propane to Propylene over Pt/Nb-modified Al₂O₃ Catalyst

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The application of Pt-based catalyst in propane dehydrogenation (PDH) was restricted by low propylene selectivity, metal sintering and carbon deposition. It is reported that the performance of catalyst is strongly related to the electronic and geometric properties of the Pt particles and the acidity of the support. Herein, we report that niobium-modified alumina supported platinum catalyst exhibits high propylene selectivity and superior stability. A high conversion of 28.8 % and a high propylene selectivity above 96 % are achieved over Pt/Nb1Al2-O catalyst for propane dehydrogenation at 600 °C after 8 h in a fixed bed reactor. Consecutive dehydrogenation-regeneration operations showed that the stability of Pt/Nb1Al2-O was really higher than that of Pt/Al₂O₃. NH₃-TPD reveals that the strong acidity is decreased, while the medium acidity is increased after introducing niobium in Al₂O₃, which may be attributed to the formation of new acid sites, probably Lewis acid sites from niobium oxide species. CO-adsorbed FTIR, CO chemisorption, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) reveal that the enhancement of electron density and the decrease of dispersion of Pt particles after the introduction of Nb, which is beneficial for inhibiting the by-reactions (carbon formation and C–C bond cleavage).

1. Introduction

As mining shale gas technology matures, many efforts have been dedicated to find efficient catalysts for propylene production via propane dehydrogenation (PDH).¹⁻⁸ However, the PDH reaction is highly endothermic and high reaction temperature is essential, which would result in the major challenges of undesired reactions, such as hydrocarbon cracking and coke formation.^{9,10} Compared with other noble metals, Pt is the only noble metal utilized in commercial PDH process due to its superior activity in C-H bond activation and low activity for C-C bond cleavage.^{11,12} However, the selectivity to propylene still need to be enhanced and the coke formation as well as the sintering of Pt particles need prevented.¹³⁻¹⁶ It is found that the electronic state and geometric properties of Pt have an effect on the reaction.^{9,12} The higher electron density of Pt is benefit to weakening the adsorption of olefins, thereby reducing coke formation. The small particle sized Pt favors the dehydrogenation reaction, but it is also beneficial to some undesired side reactions, such as cracking of C-C bond, isomerization, and coke formation.¹⁷ So, there is still no general consensus regarding the suitable dispersion and particle size of platinum for PDH process. It is reported that the dispersion and

stability of Pt particle is closely related to the support,^{18,19} and in addition, the acidity of support also influences the performance, because higher acidity will lead to serious coke formation.^{20, 21}

Alumina is widely used as the carrier in Pt-based catalyst in PDH reaction due to its high thermal stability and large surface area.^{19,22} However, unsatisfactory catalytic performance was got over the solely Pt/Al_2O_3 catalyst because of the catalyst acidity of Al_2O_3 and metal sintering. In order to reduce support acidity and suppress the sintering of Pt particles, Sn, In, Cu and alkaline metals (Li, Na, and K) are introduced as auxiliary agents into Pt/Al_2O_3 and higher catalytic stability was got over these catalysts.^{21,23,24} So, suitable promoters are necessary for traditional Pt/Al_2O_3 to get excellent catalytic performance.

Nb-containing catalysts show excellent performance in the oxidative dehydrogenation (ODH) of alkanes.²⁵⁻²⁸ For example, Lemonidou *et al.* developed a kind of Ni-Nb-O oxide catalyst, which is highly active and selective in ODH.²⁶ MoVTeNbO catalysts, prepared by López Nieto et al., showed high selectivity in the ODH of ethane.²⁷ Lewis acid was proven to be benefit for the dehydrogenation of isobutane *via* promoting the C-H activation and accelerating H₂ desorption, thus leading to an improved reactivity.^{29,30} So, we propose that the Nb-containing catalysts, which were reported as catalysts with high Lewis acidity,³¹ would be a promising candidate for achieving a good performance in PDH process.

In this work, niobium was introduced into traditional Pt/Al_2O_3 catalyst by two-steps. First, the NbAl-O supports with different Nb/Al ratios were synthesized by a co-precipitation method, and then the Pt/NbAl-O catalysts were prepared by an incipient wetness impregnation method. It was found that, the selectivity

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> to C_3H_6 was improved greatly after introducing Nb into Al_2O_3 . After systematic characterizations, we find that, compared with Pt/Al_2O_3 , the Pt/NbxAly-O catalysts have higher Pt electron density and the smaller amount of low-coordinated Pt, which could reduce coke formation, weaken the deep C-C bond cracking and enhance the catalysts stability. In addition, the decrease of the strong acidity of the catalyst also inhibits carbon deposition.

2. Experimental

2.1 Materials and methods

Materials

Propane, C_3H_8 (99.9%) was obtained from Shanghai Chunyu Special Gas Co., Ltd. Ammonium niobate(V) oxalate hydrate was bought from Dibo Reagent Co., Ltd. Aluminum nitrate nonhydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Pt (NO₃)₂ was bought from Heraeus Materials Technology Shanghai Co., Ltd. NaOH was obtained from Shanghai Titan Scientific Co., Ltd. All chemicals were of analytical grade and used without further purification.

Synthesis of Pt/Al₂O₃ and Pt/NbAl-O and catalysts

The supports were prepared by precipitation method. In a typical synthesis, Ammonium niobate(V) oxalate hydrate and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 50 mL of water, respectively. Then the solutions of aluminum nitrate and ammonium niobium oxalate were simultaneously dropped into a 250 mL beaker and the system was heated in a 70 °C oil bath. The pH of the system was maintained at 7 by continuously dropping the aqueous solution of NaOH. After stirring and heating for 1 h, the solid formed was filtered, washed with distilled water and dried at 50 °C for 12 h and 100 °C for 12 h, respectively. After calcining at 600 °C, the NbxAly-O supports were obtained, where x/y indicates the mass ratio of Nb/Al.

The $\gamma\text{-}Al_2O_3$ support was prepared in the same way by using Al (NO_3)_3·9H_2O as the only precursor.

Incipient wetness impregnation method was adopted for the catalyst preparation. In a typical case, a certain amount of deionized water was added to 0.4 mL of the aqueous solution of Pt $(NO_3)_2$ (0.025 g/mL Pt). Subsequently, 1 g of support was added to the above solution and stirred to obtain the precursor. The Pt-based samples were obtained after drying (50 °C for 12 h, and 100 °C for 12 h) and further calcination at 450 °C for 5 h in air.

Material characterization

Powder X-ray diffraction (XRD) patterns were recorded with a D8 Focus diffractometer by using Cu K α 1 (λ = 0.15406 nm) radiation. The operation condition was 40 kV and 40 mA.

Scanning transmission electron microscopy (STEM) characterization was performed using ThermoFisher Talos F200X. High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the Pt, Nb and Al content by

using an Agilent 725ES. A Micromeritics ASAP 2020 A sorption analyzer was used for the nitrogen adsorption/desorption measurements. Before measuring at -196 °C, the samples were degassed at 200 °C for 6 h. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) equation. The CO chemisorption was performed on a Huasi DAS-7200 automatic chemisorption system at room temperature (CO: Pt = 1:1).

 H_2 temperature-programmed reduction (H_2 -TPR) was conducted on a Huasi DAS-7200 automatic chemisorption system. Before each measurement, to remove the physically adsorbed species on the surface of the catalyst, the samples were pretreated by using pure Ar at 150 °C for 1 h. After cooling down to room temperature, the samples were heated to 800 °C with a 10 °C·min⁻¹ ramp in 10% H_2 /Ar flow.

 $\rm NH_3$ -TPD was carried out in an apparatus (PX200, Tianjin Golden Eagle Technology Co. Ltd.) equipped with a thermal conductivity detector (TCD). The detailed experimental procedures can refer to our previous work²⁵ except to change the weight of samples from 100 mg to 200 mg.

The diffuse reflectance infrared Fourier transform spectra (DRIFTS) of CO-adsorption were measured on a Nicolet Model iS-50 FT-IR spectrometer equipped with an MCT/A detector. For all of the CO-adsorption DRIFTS measurements, the catalyst was reduced in situ in a flow of 5 % H_2 /Ar at 600 °C and then flushed in Ar flow for 10 min at 600 °C, followed by cooling to 25 °C. Then, a flow of CO (30 mL/min) was introduced into the catalyst cell, and the DRIFTS were collected.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Escalab 250 Xi system with Al K α radiation operated at 250 W. The C 1s level at 284.6 eV as an internal standard was used to calibrate the binding energy. X-ray adsorption fine structure measurements (XAFS) were conducted at the beamline 44A of Taiwan Photon Source, National Synchrotron Radiation Research Center in Taiwan. XAFS measurements were conducted for the Pt L3-edge in fluorescence mode. Before the measurements of XPS and XANS, the samples were reduced at 600 °C for 1 h under 5 % H₂/Ar, cooled down to room temperature, then purged with N₂ for 1h, and finally transferred to bottles and sealed in glove box for use.

The electron paramagnetic resonance (EPR) spectra were measured at -196 °C by using a Bruker A300 spectrometer. Thermogravimetric analysis (TG/DTA) was performed on a PerkinElmer Pyris Diamond under air with a heating rate of 10 °C·min⁻¹.

C₃H₆-TPD was carried out on a Huasi DAS-7200 automatic chemisorption system with MS to determine the desorption energy of C₃H₆. Prior to C₃H₆ adsorption, the sample (0.2 g) was reduced with 5 % H₂/Ar at 600 °C for 1 h, and C₃H₆ (99.5%) was adsorbed for 1 h after cooling to 50 °C. After purging He (30 mL/min) for 2 h, the temperature was ramped up to 800 °C with a rate of 10 °C/min.

Catalytic reactions

The PDH reaction was conducted in a continuous flow fixed-bed reactor with a 6 mm inner diameter. Prior to the test, 0.11 g of catalyst with 40–60 mesh was in situ activated at 600 $^{\circ}$ C for 1 h

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with H₂ (H₂/N₂=1:4) under atmospheric pressure. After reduction, the reactant gas mixture (C₃H₈/H₂/N₂=1:1:3) was introduced through the catalytic bed at 30 mL·min⁻¹ and the propane weight hourly space velocity (WHSV(C₃H₈), grams of propane fed per gram of catalyst per hour) is 6 h⁻¹. The PDH process was conducted at 600 °C under atmospheric pressure, and the reactor effluent was separated in a phase separator and analyzed by online gas chromatography equipped with a flame ionization detector (FID). The blank experiment was investigated by running reactions at normal temperature, and the influence could be neglected. The conversion of propane (C₃H₈) and selectivity to the products (C_xH_y: C₃H₆, C₂H₆, C₂H₄, and CH₄), were calculated using the following equations:

$$Conv (\%) = \frac{[FC^{3}H^{8}]in - [FC^{3}H^{8}]out}{[FC^{3}H^{8}]in} * 100 \quad (1)$$

Sel (%) = $\frac{n_{i} * [F_{i}]out}{\sum n_{i} * [F_{i}]out} * 100 \quad (2)$

where *i* represents the hydrocarbon product in the effluent gas, n_i is the number of carbon atoms of component *i*, and F_i is the corresponding flow rate.

3. Result

The XRD diffraction was used to analyze the phase composition of the samples with different Nb content, and the results are shown in Figure 1. It is found that Al_2O_3 shows broad peaks at 39.5°, 45.8°, 66.8° and 85.0°, assigning to the γ - Al_2O_3 phase (PDF No. 29-0063), while the Nb₂O₅ shows diffraction peaks centered at 22.6°, 28.4°, 36.6°, 46.1° and 55.1°, which corresponds to TT-Nb₂O₅ (pseudohexagonal Nb₂O₅) phase (PDF no. 30-0873). Interestingly, the NbAl-O oxides show amorphous phases except Nb1Al8-O, which is close to γ - Al_2O_3 phase. The absence of the diffractions of γ - Al_2O_3 and TT-Nb₂O₅ suggests that the coordination and crystallinity of oxides were changed after mixing Nb and Al together. After loading with Pt, the XRD patterns are also given and present in Figure S1. It is hardly seen the diffraction peaks of Pt in Figure S1, indicating that very small Pt particles are dispersed on all supports.

Table 1. Element contents, specific surface area and Pt dispersion.



Figure 1. XRD patterns of various supports.



Figure 2. Typical HAADF-STEM images of (a) Pt/Al_2O_3 , (b) Pt/Nb1Al2-O. The insets show the size distribution of the two catalysts.

The composition of various catalysts was measured by ICP and the data are collected in Table 1. It shows that the mass ratio of element of the resultant catalysts is in line with the initial composition. N₂ adsorption was used to measure the surface area and the information were also summarized in Table 1. It shows the specific surface area first increases and then decreases. For Pt/Nb1Al2-O, the specific surface area is 157 m²g⁻¹.

Catalysts	Pt (wt%)	Al (wt%)	Nb (wt%)	S _{BET} (m2g-1)	D.P. (%)	d ^a (nm)
1%Pt-AI2O3	0.94	53	-	247	68.4	1.65
1%Pt-Nb1Al8-O	0.93	38	4.9	270	52.3	2.16
1%Pt-Nb1Al2-O	0.92	29	16	157	54.7	2.06
1%Pt-Nb1Al1-O	0.89	24	22	100	35.2	3.21
1%Pt-Nb2O5	0.93	-	68	25	27.9	4.05

Notes: a: d means the particle size of Pt estimated from dispersion. The calculation formula is d (nm)=1.13/dispersion.

HAADF-STEM imaging was utilized to investigate the Pt particle size and dispersion of the two representative catalysts. As shown in Figure 2, tiny Pt nanoparticles showing higher Z-contrast were observed over Pt/Al_2O_3 and Pt/Nb1Al2-O samples, indicating the high dispersion of Pt particles in these two catalysts. The average size of Pt particles of Pt/Al_2O_3 and Pt/Nb1Al2-O is 1.30 nm and 1.50 nm, respectively. To measure Pt dispersion, CO-pulse adsorption was employed and the results were also collected in Table 1. It is found that the dispersion of Pt on Pt/Al_2O_3 catalyst was 68.4 %, while it is 54.7 % over Pt/Nb1Al2-O catalyst.

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59 60 The reduction of the supported Pt catalysts, as well as the interaction of Pt with support was examined by using H₂-TPR technique, and the results were present in Figure 3. It can be seen two reduction peaks appeared over all catalysts. The former one appears at between 200 to 300 °C, while the latter exists between 350 to 450 °C. These two peaks are assigned to (i) the reduction of weakly interacted Pt species, and (ii) the reduction of Pt species interacted strongly with alumina support.³²⁻³⁵ Both two peaks slightly shift to higher temperature with increasing Nb content, suggesting that interaction was enhanced after introducing niobium, which would help to curb the sintering of Pt particles and improve the catalyst stability.

The PDH reaction was carried out at 600 °C in a fixed reactor and the results over above catalysts were shown in Figure 4 and Figure S2. Figure 4a shows the time-on-stream of the propane conversion over different catalysts. The highest conversion was got over Pt/Al₂O₃ catalyst, which is around 32 % after 8 h. However, low selectivity (< 80 %) to C₃H₆ and poor stability were observed over Pt/Al₂O₃ catalyst (Figure 4b). It is reported that the smaller particle sized Pt and higher metal dispersion favor the dehydrogenation reaction, but they are also beneficial to some undesired side reactions, such as the cracking of C-C bond and coke formation. In addition, the strong acidity of Al₂O₃ would also lead to coke formation, this will be discussed later. Hence, a high C_3H_8 conversion but low C_3H_6 selectivity was got over Pt/Al₂O₃ catalyst. For Nb-containing catalysts, although the conversion decreases with the increase of Nb content, the selectivity is higher and reached 96 % over Pt/Nb1Al2-O catalyst. So, we finally choose Pt/Nb1Al2-O as the best catalyst, because of the high stability (deactivation rate parameter, κ_d =0.0520), higher conversion (28.8 %) and highest selectivity (96.0 %) (Table S1). The following characterizations are also focused on Pt/Nb1Al2-O and Pt/Al₂O₃ catalysts. The selectivity to byproducts (CH₄, C₂H₆ and C₂H₄) was given in Figure S3 have shown that C-C bond cleavage is greatly reduced (CH₄ yield from 10% over Pt/Al₂O₃ to 3% over Pt/Nb1Al2-O) after the introduction of The catalytic performance during consecutive Nb. dehydrogenation-regeneration operations over Pt/Nb1Al2-O and Pt/Al₂O₃ catalysts was also carried out and present in Figure 5. It is found that the activities both decreased, but compared with Pt/Al_2O_3 , better catalytic stability and higher C_3H_6 selectivity were still obtained over Pt/Nb1Al2-O catalyst. The characterization performed on the spent catalyst (Figure S4-7) indicated the particle sintering for both Pt/Al₂O₃ and Pt/Nb1Al2-O. During the reaction, the Pt particles of Pt/Al₂O₃ gradually aggregate to 8.65 nm (after 1 reaction cycle) and 12.17 nm

(after 3 reaction cycles), which explains the determined where the second states of C₃H₆ selectivity over Pt/Al₂O₃. For Pt/Nb1Al2-O, the Pt particle sizes are 7.70 nm and 9.53 nm after 1 reaction cycle and 3 cycles, respectively. The slower particle aggregation means the particle stability is improved by introducing Nb. However, the anti-sintering ability of Pt/NbAl-O still required to be strengthened by adding other promoters.



Figure 3. H₂-TPR profiles of Pt/Al₂O₃ and Pt/NbxAly-O catalysts.



Figure 4. The conversion of C_3H_8 (a) and the selectivity to C_3H_6 (b) over various catalysts for PDH. Catalytic conditions: atmospheric pressure, 600 °C, $C_3H_8/H_2/N_2 = 1/1/3$, the total flow rate is 30 mL/min. WHSV of propane = 6 h⁻¹ and 110 mg of catalyst.

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Figure 5. The C_3H_8 conversion and C_3H_6 selectivity over Pt/Nb1Al2-O and Pt/Al₂O₃ catalyst during consecutive dehydrogenation-regeneration operations.

Reaction conditions: T=600 °C , WHSV=6 h⁻¹, N₂:H₂:C₃H₈=3:1:1. After each PDH run, the catalyst was regenerated by burning coke at 600 °C in flowing air for 2 h and then by H₂ reduction at 600 °C for 1 h.



Figure 6. NH3-TPD profiles of Pt/Al₂O₃ and Pt/Nb1Al2-O catalysts.

4. Discussion

It was reported that beside the properties of Pt, the acidity of the catalyst also influences the catalytic performance, so the influence of acidity was first discussed. NH_3 -TPD was carried out to measure the amount of acid and acid distribution, which were shown in Figure 6. It is well known that the peaks of NH_3 desorption around 120-200 °C, 200-300 °C and above 300 °C are regarded as the weak, medium, and strong acid sites,

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respectively.³⁶ The NH₃-TPD profiles in Figure 6 and the calculated amount of each acid site listed in Table S2, both show that the amounts of strong acids decrease, while the medium acids increase significantly after introducing Nb into the Al_2O_3 . The increased medium acids sites is Lewis acid come from NbO_x species as shown in Py-FTIR (Figure S8). It is well accepted that the strong acid sites of the catalyst can promote the formation of coke.^{5,12} The conversion of propane looks higher over Pt/Al₂O₃ catalyst, which would be due to the deep cracking to smaller molecules and the coke formation. While Pt/Nb1Al2-O, which has less strong acid sites and higher medium acid sites, is benefit for C-H activation, but poor for carbon deposition and C-C bond cracking, thus improving the selectivity to propylene and enhancing the catalytic stability.

To further compare the carbon deposits on two catalysts, TG was used to analyze the amount of coke after PDH reaction at 600 °C for 8 h (shown in Figure S10) and found less weight loss in Pt/Nb1Al2-O (13.8 wt%) than that in Pt/Al2O3 (17.9 wt%), indicating the doping of niobium in Al2O3 really suppressed coke deposition.

The properties of Pt nanoparticles play key roles in PDH, so, CO-adsorbed FTIR was used to investigate its coordinated states. The DRIFTS spectra for CO adsorption on these three catalysts (Pt/Al2O3, Pt/Nb1Al2-O and Pt/Nb2O5) are given in Figure 7 and Figure S11, respectively. It can be seen that the CO adsorption peaks are existed at 2000 cm⁻¹ ~ 2100 cm⁻¹ for all three catalysts, which can be attributed to CO species linearly absorbed on the Pt atoms. According to the previous literature, the little peak of both two catalysts around 2080 cm⁻¹ attributes to the very high coordinated Pt sites, which was reported not favor the dehydrogenation reaction.^{12,37} For Pt/Nb₂O₅, it could be seen that there is a very large part of highly coordinated Pt sites, which was reported not favor the dehydrogenation reaction and the by-reactions (cracking of C-C bond, isomerization, and coke formation), so even though the selectivity to propylene is high, the conversion is very low. To compare the differences between Pt/Al₂O₃ and Pt/Nb1Al2-O catalysts, the linearly adsorbed CO curves were fitted and separated into four peaks. (1): CO adsorption on very highly coordinated Pt sites at some low index plane. (2): CO adsorption on high index plane of small clusters. (3) and (4): CO adsorption on low coordinated Pt sites, such as steps, edges, corners and defect sites.^{9,38,39} It could be found that after introducing Nb into the support, peak 4 (low coordinated Pt sites) decreased from 26.6 % to 14.7 % with the amount of peak 2 (high index plane of small clusters) increased. DFT calculations by Yang et al. indicate that the low coordinated Pt favors the hydrogenolysis and the side reactions (coke formation and hydrocarbon cracking).³⁷ These results mean that the doping of niobium decreased the low coordinated Pt and would prevent the hydrocarbon cracking and coke formation.

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Figure 7. CO-DRIFTs of the (a) Pt/Al₂O₃ and (b) Pt/Nb1Al2-O.

Besides support acidity and coordination state of Pt, previous reports revealed that the electron density of the Pt-based catalysts is the key for PDH process.^{9,36} To clarify the difference of the surface states of Pt after introducing Nb, XPS analysis was performed, but the signals of Al 2p and Pt 4f are overlapped (Figure S12 and S13 and discussed therein). So XAS spectra were used to identify the chemical states of Pt. Figure 8 shows the normalized X-ray absorption near-edge structure (XANES) spectra at Pt L3-edge for the catalysts and the reference spectra of Pt foil and PtO₂ powder. It can be seen that the intensities of Pt in the catalysts are all slightly higher than that of Pt foil, which



Figure 8. Normalized XANES spectra at Pt L3-edge of the Pt/Al₂O₃, Pt/Nb1Al2-O, Pt foil and PtO₂ reference.

may be due to the slight oxidation of the samples. Compared with Pt/Al_2O_3 , the intensities of Pt on Nb1Al2-O are lower, which means the higher electron density. It indicates that NbAl-O support denotes electron to Pt, which may be due to the increased oxygen vacancies (O_v) with the introduction of niobium. Therefore, EPR measurements were employed to explore the O_v of the catalysts, and the results were shown in Figure S14. For these two catalysts, there is an obviously signal with a *g* value of 2.003, which is attributed to the single electron of O_2^- radical trapped by O_v .^{40,41} The existence of Nb facilitated the generation of O_v , which transfer electrons to Pt and also generate more Lewis acid sites, finally enhanced propylene selectivity and prevent coke formation.

In order to compare the adsorption strength of catalysts to propylene, the adsorption of propylene on the catalysts were examined by the means of C_3H_6 -TPD, and the desorption profiles were presented in Figure 9. The MS signal of TPD measurements shows that the propylene adsorbed on both Pt/Al₂O₃ and Pt/Nb1Al2-O can desorb at relatively low temperature. But obviously, the desorption of C_3H_6 over Pt/Nb1Al2-O catalyst shifts to a lower temperature compared with that of Pt/Al₂O₃, which decreased from 99 °C to 80 °C. More interestingly, the peak area of C_3H_6 desorption reduced a lot on Pt/Nb1Al2-O, suggesting the weaker C_3H_6 adsorption. The TPD characterization results are in line with the TG results. Weaker interaction between the catalysts and C_3H_6 leads to the less coke formation and higher catalyst stability.

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Figure 9. C₃H₆-TPD of Pt/Al₂O₃ and Pt/Nb1Al2-O catalysts.

Based on above results and discussion, we found that compared with Pt/Al₂O₃, the decrease of strong acidity and low coordinated Pt are benefit for preventing the formation of coke and hydrocarbon cracking. In addition, the higher electron density of Pt over Pt/NbxAly-O weakens the interaction between C_3H_6 and Pt, which also lessens the formation of coke.

5. Conclusion

In summary, we prepared a novel catalyst by introducing Nb into the traditional Al₂O₃ support for the PDH reaction, in which the C_3H_8 conversion and the C_3H_6 selectivity reached 28.8% and 96.0% after 8 h, respectively. The function of Nb was investigated and found it played key roles in tuning the support acidity and Pt state. NH₃-TPD results show the reducing of the strong acid, which favors the stability of catalyst by lessening the coke formation. CO-pulse adsorption and DRIFTS for CO adsorption prove the decrease of Pt dispersion and low coordinated Pt sites, which help to avoid the C-C bond cleavage (formation of CH_4 , C_2H_6) and enhance propylene selectivity. The increase of electron density of Pt particles which was proven by XPS and XANES can weaken the ability to adsorb propylene and also prevent coking formation. Moreover, the fast sintering of Pt was also reduced after Nb modification. It is believed that these findings possess potentials for further design of high selectivity and stability catalysts for PDH process.

Conflicts of interest

There are no conflicts to declare.

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