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Article

Effect of pH on the catalytic performance of PtSn/B-ZrO₂ in propane dehydrogenation

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ABSTRACT

Boron-modified ZrO₂ (B-ZrO₂) was synthesized under various pH values (9, 10, and 11) and used as the supports of PtSn catalysts (PtSn/B-ZrO₂-x) for non-oxidative dehydrogenation of propane. The NH₃-TPD and pyridine IR show that only Lewis acid is present and the acid strength increases with the synthesis pH. PtSn/B-ZrO₂-10 exhibits the best catalytic performance with an initial propane conversion of 36% and a deactivation rate constant (*k_d*) of 0.0127 h⁻¹. The XPS results indicate that the electronic properties of Pt and SnO_x are affected not only by their interaction but also by the interaction with support. After a careful analysis of the oxygen storage capacity and activity in CO oxidation, it is hypothesized that the interaction between Pt and Sn becomes stronger following the order: PtSn/B-ZrO₂-9 < PtSn/B-ZrO₂-11 < PtSn/B-ZrO₂-10. The characterization with TPO and Raman on spent catalysts exhibits that more hydrogen deficient coke forms on the support and less coke deposits on the metal surface of PtSn/B-ZrO₂-10. The results reveal that the interaction between Pt and Sn is influenced by their respective interaction with the support and a moderate interaction between the metal species and the support is desired.

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1. Introduction

As one of the important basic chemicals, propylene is traditionally co-produced with ethylene from petroleum-based processes such as steam cracking or fluid catalytic cracking [1,2]. With the depleting crude oil and the discovery of large reserves of shale gas, steaming cracking of ethane with high selectivity to ethylene and negligible co-production of propylene becomes more competitive and is replacing the traditional petroleum-based processes [3]. Thus, a more economical alternative such as direct dehydrogenation of propane to propylene is desired to meet the increasing demand of propylene [4,5].

Propane dehydrogenation (PDH) has been under wide in-

vestigation and currently available catalysts include PtSn and Cr supported on Al₂O₃ [6]. Among them, PtSn-based catalyst is more environmentally benign and thus more widely used [3,7]. However, the catalyst still suffers from problems such as deactivation mainly due to carbon deposits and metal sintering, and thus frequent coke combustion in air as well as re-dispersion in Cl₂ atmosphere is required in practical process [8–10]. Protocols including improving the metal-support interaction, enhancing the interaction between Pt and Sn, and altering the acidic property of supports have been carried out in order to enhance the catalyst stability in PDH [11–14]. For example, Zhu et al. [15] reported that Sn can be selectively deposited on Pt nanoparticle surface via surface organometallic chemistry and as-obtained catalysts exhibited a remarkable activity and sta-

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bility in PDH. In addition, an improved stability was achieved by adding Mg or Zn to Al_2O_3 to eliminate acidic sites and strengthen the metal-support interaction [4,16]. It should be noted that not all kinds of acid sites are detrimental in PDH. A number of studies have shown that Lewis acid sites may facilitate the dehydrogenation reaction while Brönsted acid sites favor side reactions such as cracking and oligomerization [17–22]. This is further validated by a recent report that gallosilicate MFI zeolite with a higher concentration of strong Lewis acid sites and reduced concentration of Brönsted acid sites showed a better PDH activity and propylene selectivity [23]. Furthermore, these Lewis acid sites originating from the defect sites or coordinatively unsaturated sites can also provide anchoring sites for supported metal particles [24–26].

Notably, some oxides that can be treated to form defects are proven to be active in light alkane dehydrogenation. Rodemerck et al. [27] reported that even Al_2O_3 after reduction at 600 °C for 10 h or calcined in air at 550 °C exhibited activity for butane dehydrogenation, and the dehydrogenation activity was linearly correlated with coordinatively unsaturated Al sites (Lewis acidic sites) due to desorption of strongly bound surface OH groups in the form of water. Although that study did not identify the coordination number of such coordinatively unsaturated Al, a study by Kwak et al. [28] showed that coordinatively unsaturated Al sites produced by dehydration and dehydroxylation at high temperatures were penta coordinated, which also acted as the anchoring sites to stabilize Pt atoms. A following study by Shi et al. [29] exhibited that superior stability could be obtained by impregnating PtSn on alumina oxides rich in penta coordinated alumina. In addition, Otroshchenko et al. [30] reported that La or Y doped ZrO_2 with tiny amounts of Cu or Ru could facilitate the reduction of ZrO_2 and exhibited a competitive activity as the Cr_2O_3 -based catalyst in PDH. The active sites were proposed to be the coordinatively unsaturated Zr cation and the adjacent oxygen [31]. Recently, Otroshchenko et al. [32] reported that the synergy effects between CrO_x and coordinatively unsaturated Zr^{4+} sites favored catalysts containing much lower chromium content with superior performance in comparison to commercial $\text{K-CrO}_x/\text{Al}_2\text{O}_3$. It is also highly desirable to reduce the usage of Pt without degrading the catalytic performance. The latest generation of catalyst DeH-16 developed for UOP Oleflex process contains only 0.3 wt% Pt, 30% lower relative to previous generation catalysts. However, the catalyst stability was apt to deteriorate with decreasing Pt content [6,33].

Although extensive work on the ZrO_2 based catalyst for PDH has been conducted by BASF [34], the stability of ZrO_2 supported PtSn catalyst in dehydrogenation reaction is still poor [35,36]. Previous studies showed that the amount and strength of Lewis acid sites was enhanced while Brönsted acid sites was greatly suppressed by adding electron-deficient boron to ZrO_2 through the inductive effect [37,38]. In analogous with the case of Al_2O_3 , we can propose that ZrO_2 with a suitable amount of coordinatively unsaturated Zr sites would be an eligible candidate support for PtSn in PDH. Moreover, ZrO_2 is widely used as a support in reactions due to its high mechanical and thermal stability [39]. The synthesis pH value of support was reported

to influence the catalytic performance in PDH [14]. However, there is still no study on the influence of synthesis pH value of boron modified ZrO_2 (B- ZrO_2) on the catalytic performance in PDH.

Herein, we showed that the synthesis pH value of B- ZrO_2 has a significant effect on the catalytic performance of PtSn/B- ZrO_2 in PDH with Pt loading around 0.35 wt%. Characterizations were carried out to investigate the correlations between the structure and catalytic performance of PtSn/B- ZrO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

All chemicals are of analytical grade and purchased from Sinopharm Chemical Reagent. The previously reported method was adapted for preparation of boron modified ZrO_2 [37]. Briefly, the pH of aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.5 mol/L) and H_3BO_3 was adjusted to the desired value by dropwise addition of ammonia solution (25–28 wt%) under vigorous stirring. The pH value was monitored with a PHS-3C pH meter (Rex Instrument Factory, Shanghai, China). Then the mixture was refluxed at 100 °C for 26 h. The collection and subsequent treatment of precipitate were conducted according to the previous report [37] except that the products were calcined in flowing air at 800 °C for 5 h at a heating rate of 10 °C/min. The samples were denoted as B- ZrO_2 -x with the x representing the pH value.

PtSn/B- ZrO_2 -x samples were prepared by the incipient-wetness co-impregnation method with $\text{H}_6\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as precursors. A 3 mL ethanol solution of $\text{H}_6\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was impregnated onto 2 g B- ZrO_2 -x. Subsequently, the PtSn/B- ZrO_2 -x was kept at 40 °C for 1 h and dried at 110 °C for 12 h. Finally, the samples were calcined at 500 °C for 4 h in flowing air at a flow rate of 40 mL/min. The loadings of platinum and tin were measured to be around 0.35 wt% and 0.8 wt%, respectively, by ICP-OES.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on an Empyrean diffractometer (PANalytical) using a $\text{Cu K}\alpha$ radiation source with a scan rate of 10°/min in the 2θ range of 5°–70°. The volume fraction of monoclinic ZrO_2 was estimated according to the reported equations [40]:

$$X_m = \frac{I_m(111) + I_m(1\bar{1}\bar{1})}{I_m(111) + I_m(1\bar{1}\bar{1}) + I_t(011)} \quad (1)$$

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (2)$$

where $I_m(111)$ and $I_m(1\bar{1}\bar{1})$ are the peak intensities of the (111) and $(1\bar{1}\bar{1})$ planes of monoclinic ZrO_2 , respectively, and the $I_t(011)$ is the peak intensity of the (011) plane of the tetragonal ZrO_2 .

The total oxygen vacancy or oxygen storage capacity (OSC) of various samples was measured using a thermogravimetric instrument (STA 449 F3, Netzsch, Germany) by the method

adapted from the previous report [41]. The sample was first heated up to 800 °C in N₂ to release oxygen, then cooled to 40 °C in air, and again heated to 800 °C in N₂. The weight loss during the second run was employed to represent the OSC expressed in μmol O₂/g catalyst.

The concentration of B, Pt, and Sn was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a PerkinElmer apparatus Optima 7300 DV.

Nitrogen physisorption was performed with a Quantachrome QUADRASORB SI system at −196 °C. All samples were outgassed at 300 °C for 6 h before measurement. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) equation using the adsorption data ($P/P_0 = 0.05\text{--}0.3$). The total pore volume was calculated at the largest point of relative pressure P/P_0 . The average pore size was calculated by the BJH method from the nitrogen adsorption data.

NH₃-TPD was performed on a Micromeritics Auto Chem 2910. The PtSn/B-ZrO₂-*x* catalyst samples were pre-reduced at 500 °C for 1 h in 10 vol% H₂/Ar before NH₃ adsorption at 100 °C.

Pyridine adsorption FTIR infrared (Py-IR) spectroscopy was carried out on a Bruker Optics XF808-04 Fourier transform infrared spectrometer (FTIR) with pyridine as a probe molecule. The self-supported sample wafer was kept at 400 °C in vacuum for 1 h before absorption of pyridine at room temperature. The signal was collected at room temperature after evacuation at 150 °C for 30 min in vacuum.

CO-IR was carried out on a Bruker TENSOR 27 spectrometer. The self-supported sample wafer was in situ reduced at 500 °C for 1 h in 100% H₂. The spectroscopy of hydroxyl groups on reduced samples was obtained at room temperature after purge in N₂ for 30 min. The FTIR spectra of CO on reduced products were collected after saturation adsorption of CO and subsequent evacuation in N₂ for 30 min, respectively.

XPS was performed on a Thermo ESCALAB 250Xi with Al K_α as X-ray source. The binding energy was calibrated using C 1s at 284.6 eV. For characterization of reduced samples, the sample was in situ reduced at 500 °C for 1 h in 100% H₂ atmosphere.

The amount of coke was characterized by thermogravimetric analysis (TG) on a thermogravimetric instrument (STA 449 F3, Netzsch, Germany). Temperature-programmed oxidation (TPO) was carried out on a home-made apparatus equipped with an on-line mass spectrometer (MS) to monitor the CO₂ formation. Raman spectroscopy was collected on a NanoWizard Ultra Speed & inVia Raman.

2.3. Catalytic reaction

2.3.1. CO oxidation test

Before the catalytic activity test, the catalysts (20 mg) were pre-reduced at 500 °C for 1 h. After cooling to room temperature in Ar gas (30 mL/min), a gas mixture of 1% CO, 20% O₂, and 1% N₂ balanced with He was fed at a flow rate of 10 mL/min. The catalytic performance was investigated by temperature-programmed mode at a rate of 1 °C/min. The efflu-

ents were analyzed with an online micro-gas chromatograph (Agilent GC-490) equipped with a thermal conductivity detector (TCD) with a 5 Å molecular sieve column.

2.3.2. PDH test

The reaction was carried out at 550 °C under atmospheric pressure in a quartz microreactor with an inner diameter of 8 mm. 200 mg catalyst was loaded and heated to 500 °C in Ar (30 mL/min) within 48 min, kept at 500 °C in Ar (30 mL/min) for 15 min, flushed with Ar (50 mL/min) for 10 min and then reduced at 500 °C for 1 h in 100% H₂ (30 mL/min) prior to reaction. The feed gas contained 10% propane, 10% H₂, and 80% N₂. The weight hourly space velocity (WHSV) of propane was 3 h^{−1}. The product was analyzed with an online gas chromatograph (GC, Agilent 7890A) equipped with an FID detector with an HP-AL/S column. The conversion of propane and the product selectivity were calculated following Eqs. (3) and (4), respectively.

$$\text{Conv.} = \frac{F_{\text{propane}}^{\text{inlet}} - F_{\text{propane}}^{\text{outlet}}}{F_{\text{propane}}^{\text{inlet}}} \times 100\% \quad (3)$$

$$S(i) = \frac{N_i^{\text{carbon}} \times F_i^{\text{outlet}}}{\sum (N_i^{\text{carbon}} \times F_i^{\text{outlet}})} \times 100\% \quad (4)$$

where *i* represents the hydrocarbon product in the effluent gas, and *N_i* and *F_i* represent the carbon number and flow rate of corresponding product *i*, respectively. The deactivation rate constant (*k_d*, h^{−1}) was employed to evaluate the catalyst stability and was calculated as follows [29].

$$k_d = \frac{\ln[(1 - X_{\text{final}})/X_{\text{final}}] - \ln[(1 - X_{\text{initial}})/X_{\text{initial}}]}{t} \quad (5)$$

where *X_{initial}* and *X_{final}* represent the conversion of propane measured at 5 min and 5 h of catalytic test, respectively, and *t* is the reaction time of 5 h.

3. Results and discussion

3.1. Results

The N₂ adsorption-desorption isotherms of all samples shown in Fig. 1 are characteristic type IV with H3 hysteresis loop, indicating the presence of nonuniform mesopores formed by aggregates of particles. As presented in Table 1, the specific

Fig. 1. N₂ adsorption-desorption isotherms of B-ZrO₂-*x*.

Table 1
Characteristics of B-ZrO₂ supports prepared at different pH values.

Sample	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	d_{pore} (nm)	m-ZrO ₂ phase (%)	OSC (μmol O ₂ /g catalyst)	NH ₃ -TPD (NH ₃ mole- cules/nm ²)
B-ZrO ₂ -9	51.1	0.25	25.6	41.3	159.5	0.18
B-ZrO ₂ -10	50.6	0.25	25.7	30.0	140.5	0.21
B-ZrO ₂ -11	42.3	0.21	18.7	18.7	191.0	0.30

surface area (S_{BET}), pore volume (V_{pore}), and the average diameter size (d_{pore}) are the lowest for B-ZrO₂-11.

Fig. 2 shows the XRD patterns of the bare supports synthesized at different pH values and the corresponding PtSn/B-ZrO₂-*x* samples. Besides the peaks attributed to tetragonal ZrO₂ (t-ZrO₂), peaks at $2\theta = 28^\circ$ and 31° assigned to monoclinic ZrO₂ (m-ZrO₂) are also observed, which is different from the previous report [37]. This may be due to the digestion time shorter than 48 h or prolonged exposure to water or vapor, which promotes the phase transformation during cooling and purification [42,43]. The volume fraction of m-ZrO₂ formed at different pH was calculated and summarized in Table 1. It can be seen that the content of m-ZrO₂ decreases with pH value. The absence of Pt and Sn diffraction peaks indicates their high dispersion or their sizes below the XRD detection limitation. Compared with pure B-ZrO₂, it is clear that the impregnation of PtSn and subsequent calcination lead to reduced fraction of m-ZrO₂ and increased fraction of t-ZrO₂ for all samples (Table S1), suggesting the occurrence of phase transformation from m-ZrO₂ to t-ZrO₂. It has been reported that the presence of oxygen vacancy was vital for the thermal stability of t-ZrO₂ [44]. The inverse phase transformation taking place after impregnating PtSn and subsequent calcination may be triggered by the creation of oxygen vacancy due to the metal-support interaction [45,46]. The existence and changes of oxygen vacancies or defects before and after impregnating PtSn on B-ZrO₂ was further corroborated via the thermogravimetric analysis [47]. The oxygen storage capacity (OSC) is 394.1, 407.7, and 376.8 μmol O₂/g catalyst for PtSn/B-ZrO₂-9, PtSn/B-ZrO₂-10, and PtSn/B-ZrO₂-11, respectively, which are obviously higher than those of bare B-ZrO₂-*x* (Table 1 and Table S1). A previous study reported that more anionic defects were generally found on m-ZrO₂ than t-ZrO₂ [48]. However, this is not observed in the

Fig. 2. XRD patterns of various samples.

present study, indicating that the phase of ZrO₂ may not be the dominant factor affecting the vacancy concentration.

The acidity of B-ZrO₂ and corresponding supported PtSn samples was investigated by NH₃-TPD. As shown in Fig. 3, the desorption temperature increases from 174 to 218 °C, indicating that stronger acid sites are generated under a higher pH value. The apparent NH₃ surface density (number of NH₃ molecules adsorbed per nm²) of B-ZrO₂-9 and B-ZrO₂-10 is close while lower than that of B-ZrO₂-11 (Table 1). However, upon impregnation with PtSn, the desorption temperature decreases for PtSn/B-ZrO₂-10 and PtSn/B-ZrO₂-11 while increases for PtSn/B-ZrO₂-9 compared with the corresponding supports. Additionally, the apparent NH₃ surface density of PtSn/B-ZrO₂-10 and PtSn/B-ZrO₂-9 increases and that of PtSn/B-ZrO₂-11 reduces compared with the corresponding support (Table S1).

The nature of acid sites is further studied by IR using pyridine as a probe molecule (Py-IR). As shown in Fig. 4, the typical absorbance band at 1540 cm⁻¹ ascribed to Brönsted acid is absent on all samples, which is in line with previous results [37]. The band at 1610 cm⁻¹ should be attributed to pyridine adsorbed on the medium strength Lewis acid sites namely coordinatively unsaturated Zr⁴⁺ cations [49,50], while the 1630 cm⁻¹ band to the stronger Lewis acid sites [50]. The band at 1580 cm⁻¹ can be assigned to physically adsorbed pyridine, and the 1460 cm⁻¹ to the coordinatively bonded pyridine [37]. The areas of 1610 and 1630 cm⁻¹ were integrated to show the differences in number of medium strength and strong Lewis acid

Fig. 3. NH₃-TPD of B-ZrO₂-*x* and in situ reduced PtSn/B-ZrO₂-*x*.

Fig. 4. IR spectra of pyridine adsorption on B-ZrO₂-x.

sites on various supports, respectively. It can be seen from Table 2 that the number of strong and medium strength Lewis acid sites follows the order B-ZrO₂-9 $\approx$ B-ZrO₂-10 < B-ZrO₂-11. It should be noted that the number of strong Lewis acid sites on B-ZrO₂-9 and B-ZrO₂-10 is similar, contradicting the acidity strength determined by NH₃-TPD. This might be attributed to the weak acidity and similar amount of acid sites on B-ZrO₂-9 and B-ZrO₂-10, as well as the semi-quantitative quality of Py-IR.

CO-IR was carried out to get further insight into the property of reduced PtSn/B-ZrO₂. Fig. 5a shows that the band centered around 2174 cm⁻¹ and the one centered around 2115 cm⁻¹ are observed for all samples, which can be attributed to gas-phase CO. The possible bands due to CO on Pt or PtO should be overlapped by the broad band centered at 2115 cm⁻¹ [51]. Notably, it can be seen that typical bands ascribed to surface hydroxyl groups or adsorbed water are absent in IR spectra of reduced samples (Fig. S2), which is a good indicator of the dehydroxylation or dehydration during reduction [52]. Then it would be understandable that the common bands in the range of 1200–1800 cm⁻¹ ascribed to CO interacting with basic or acidic OH groups are not observed [53]. Moreover, the weak peak at 1691 cm⁻¹ is therefore more likely assigned to CO adsorbed at the Pt-ZrO₂ interface other than ionic bicarbonate species (i-HCO₃⁻) [54,55].

IR spectra of CO adsorption on reduced samples after evacuation for 30 min are shown in Fig. 5b. The main bands at 2174 and 2115 cm⁻¹ disappear after evacuation at room temperature. The band in the range of 2076–2081 cm⁻¹ is ascribed to CO linearly adsorbed on highly coordinated Pt and the blue shift with increasing pH value is discernible [56]. The absence

Fig. 5. CO-IR spectra of reduced PtSn/B-ZrO₂-x after saturated adsorption of CO (a) and after evacuation for 30 min (b).

of 1800 cm⁻¹ band (characteristic CO bridge adsorbed on Pt particles) suggests a high dispersion of Pt [56].

The XPS spectra of the Pt 4f and Sn 3d for reduced catalysts are presented in Fig. 6 and Fig. 7, respectively. The fitting spectra and semi-quantitative results are summarized in Table 3. As shown in Fig. 6, the Pt 4f XPS spectra can be deconvoluted into two doublets with the Pt 4f_{7/2} binding energies (BEs) of ca. 71.50–71.67 eV and 72.46–72.68 eV attributed to Pt⁰ and Pt²⁺, respectively [57,58]. It can be seen from Table 3 that the percentage of Pt²⁺ for PtSn/B-ZrO₂-9, PtSn/B-ZrO₂-10, and PtSn/B-ZrO₂-11 are 8.3%, 8.3%, and 15.1%, respectively, indicating the stronger interaction between Pt species and B-ZrO₂-11, which may hinder the reduction of Pt oxides [51]. The binding energy of Pt⁰ 4f_{7/2} as shown in Table 3 follows the order PtSn/B-ZrO₂-9 $\approx$ PtSn/B-ZrO₂-10 < PtSn/B-ZrO₂-11, suggesting that most electron deficient Pt species formed on PtSn/B-ZrO₂-11.

Fig. 7 shows the Sn 3d spectra of PtSn/B-ZrO₂-x catalysts. The fitting spectra and semi-quantitative results are compiled in Table 3. There are two doublets with the Sn 3d_{5/2} BEs of ca. 484.78–484.89 eV and 486.77–486.96 eV attributed to Sn⁰ and Sn²⁺/Sn⁴⁺, respectively [59]. However, it is difficult to differentiate the Sn²⁺ and Sn⁴⁺ because of the close binding energy between them [59]. As presented in Table 3, the percentages of Sn²⁺/Sn⁴⁺ are 91.9%, 94.7%, and 94.8% for PtSn/B-ZrO₂-9, PtSn/B-ZrO₂-10, and PtSn/B-ZrO₂-11, respectively. This indicates that ZrO₂ doped by even a small amount of boron in this

Table 2

Integral absorption band areas in the Py-IR spectra of B-ZrO₂-x. The numbers in the brackets represent the integrated areas of absorption band averaged by the specific surface areas of the corresponding sample.

Sample	A (1630 cm ⁻¹) (a.u.)	A (1610 cm ⁻¹) (a.u.)	A (1460 cm ⁻¹) (a.u.)
B-ZrO ₂ -9	0.78 (0.015)	0.14 (0.0027)	—
B-ZrO ₂ -10	0.67 (0.013)	0.10 (0.0020)	—
B-ZrO ₂ -11	1.30 (0.03)	0.36 (0.0085)	0.13

Fig. 6. XPS spectra of Pt species in reduced PtSn/B-ZrO₂-x. Fig. 7. XPS spectra of Sn species in reduced PtSn/B-ZrO₂-x.

study stabilizes the oxidation state of Sn and this differs from previous research that the interaction between pure ZrO₂ and Sn is weak resulting in more Sn⁰ [35,36].

The results of CO oxidation on different pre-reduced PtSn/B-ZrO₂-x under atmospheric pressure as a function of temperature are shown in Table 4. The temperature for half conversion of CO ($T_{50\%}$) on PtSn/B-ZrO₂-10 is the lowest at 160 °C while it is similar on PtSn/B-ZrO₂-9 and PtSn/B-ZrO₂-11 (170 and 168 °C, respectively, Table 4). The temperature for full CO conversion ($T_{100\%}$) follows the order PtSn/B-ZrO₂-10 < PtSn/B-ZrO₂-11 < PtSn/B-ZrO₂-9 (Table 4).

Fig. 8 presents catalytic performance for PDH on PtSn/B-ZrO₂-x as a function of reaction time. The initial propane conversion is 31.5% for PtSn/B-ZrO₂-9 and 36.0% for PtSn/B-ZrO₂-10 whereas it is 34.8% for PtSn/B-ZrO₂-11. The propylene selectivity is the highest on PtSn/B-ZrO₂-9 and the lowest on PtSn/B-ZrO₂-10. The most stable catalyst is obtained on PtSn/B-ZrO₂-10 with the deactivation rate constant (k_d) of 0.0127 h⁻¹. In comparison, PtSn/B-ZrO₂-9 exhibits a k_d of 0.0997 h⁻¹ and PtSn/B-ZrO₂-11 of 0.0272 h⁻¹. Moreover, com-

pared to the industrially relevant reference catalyst using Al₂O₃ as the support, it can be seen that the conversion on PtSn/B-ZrO₂-10 is close to that over 0.5 wt% PtSn/Al₂O₃ and the stability of PtSn/B-ZrO₂-10 is better than that of 0.35 wt% PtSn/Al₂O₃ (Fig. S3).

It is notable that the specific activity of C₃H₆ formation of PtSn/B-ZrO₂-10 (mol C₃H₆ formed)/(mol Pt*t(s)) is 0.374 s⁻¹, suggesting a larger specific activity of C₃H₆ formation but a lower deactivation rate constant (k_d) of PtSn/B-ZrO₂-10 than most of those catalysts listed in references [7] and [29]. Compared to recent studies on Pt-based catalysts with a similar loading around 0.35 wt%, PtSn/B-ZrO₂-10 exhibits an excellent stability in PDH (Table S2).

The amount of coke formed on spent catalysts was evaluated by TG. The amount of coke on PtSn/B-ZrO₂-9 is 0.06%, larger than that (0.04%) on PtSn/B-ZrO₂-11. No weight loss is detected on spent PtSn/B-ZrO₂-10. It should be noted that this does not mean no coke formation on PtSn/B-ZrO₂-10. As more oxygen vacancy sites on PtSn/B-ZrO₂-10, the weight augment by the oxygen replenishment may outnumber the limited weight loss due to coke combustion in oxidizing environment.

TPO was carried out and the evolution of CO₂ was recorded by MS to gain insights into the location of coke depositions [60].

Table 3

XPS binding energies and distribution of Pt and Sn with different oxidation states in reduced PtSn/B-ZrO₂-x.

Catalyst	Pt 4f _{7/2} BE (eV)		Sn 3d _{5/2} BE (eV)	
	Pt ²⁺	Pt ⁰	Sn ^{2+/4+}	Sn ⁰
PtSn/B-ZrO ₂ -9	72.68 (8.3%)	71.50 (91.7%)	486.52 (91.9%)	484.55 (8.1%)
PtSn/B-ZrO ₂ -10	72.46 (8.3%)	71.52 (91.7%)	486.56 (94.7%)	484.49 (5.4%)
PtSn/B-ZrO ₂ -11	72.67 (15.1%)	71.67 (84.9%)	486.88 (94.8%)	484.73 (5.3%)

Table 4

The temperature for full and half conversion of CO oxidation reaction on pre-reduced PtSn/B-ZrO₂-x.

Catalyst	$T_{50\%}/^{\circ}\text{C}$	$T_{100\%}/^{\circ}\text{C}$
PtSn/B-ZrO ₂ -9	170	183
PtSn/B-ZrO ₂ -10	160	172
PtSn/B-ZrO ₂ -11	168	177

Fig. 8. Catalytic performance of PtSn/B-ZrO₂-x in PDH. (a) Propane conversion, (b) Selectivity to propylene, (c) Deactivation rate constant.

As shown in Fig. 9, a more obvious shoulder around 285 °C is observed on PtSn/B-ZrO₂-9 and PtSn/B-ZrO₂-11 compared to PtSn/B-ZrO₂-10. Additionally, the main peak shifts from 324 °C for PtSn/B-ZrO₂-9 to 338 °C for PtSn/B-ZrO₂-10. A broad band with its maximum above 400 °C is identified for PtSn/B-ZrO₂-11. The intensity of band above 400 °C is stronger for both PtSn/B-ZrO₂-10 and PtSn/B-ZrO₂-11 than PtSn/B-ZrO₂-9.

The coke species were further characterized by Raman spectroscopy (Fig. 10). The peak centered around 1356–1329 cm⁻¹ can be attributed to the breathing mode of *sp*² in rings, generally known as disordered graphite (D band) [61,62]. The considerable band shift indicates the chemical changes of formed coke. The peak at 1528 cm⁻¹ with a shoulder around 1552 cm⁻¹ should be ascribed to conjugated olefinic species or polyenes, which were possibly aromatics precursors [62,63]. Bands at 1587 cm⁻¹ may be due to graphite or large polycyclic aromatics (G band) [64]. The band shifted to 1603 cm⁻¹ for both PtSn/B-ZrO₂-10 and PtSn/B-ZrO₂-11, which can be due to ring stretches of C=C chains or aromatics rings [61]. The *I*_D/*I*_G ratio of PtSn/B-ZrO₂-11 is higher than that of PtSn/B-ZrO₂-10, indicating that coke deposited on PtSn/B-ZrO₂-10 more hydrogen deficient.

3.2. Discussion

3.2.1. Possible factors affecting CO oxidation activity

Both the theoretical calculation and experimental findings support that even PtSn alloy formed by pre-reduction under-

Fig. 9. TPO profiles of the spent PtSn/B-ZrO₂-x catalysts.

went isolation into domains of Pt and Sn oxides and the CO oxidation took place right on the interface between Pt and Sn oxides [65,66]. This is plausible considering enhanced CO oxidation activity when more Sn was selectively deposited on Pt surface [15]. Notably, the role of oxygen storage capacity of various supports in CO oxidation cannot be neglected especially for possible isolated Pt particles on support in this work, as it was previously observed that CO oxidation was linearly correlated with the oxygen storage capacity [67–69]. However, no linear relation was observed between the oxygen storage capacity and the CO oxidation activity in this work. Therefore, more interfaces between Pt and Sn oxides resulting from their intimate contact are hypothesized, which may play an important role in CO oxidation and increase in the order PtSn/B-ZrO₂-9 < PtSn/B-ZrO₂-11 < PtSn/B-ZrO₂-10.

3.2.2. The possible support effect on interaction between Pt and Sn

The XPS results showed that the binding energy of Pt⁰ follows the order PtSn/B-ZrO₂-9 (BE: 71.50) ≈ PtSn/B-ZrO₂-10 (BE: 71.52) < PtSn/B-ZrO₂-11 (BE: 71.67) (Table 2), indicating

Fig. 10. Raman spectra of the spent PtSn/B-ZrO₂-x catalysts.

the most electron deficient Pt on PtSn/B-ZrO₂-11. The positive effect of Sn on Pt in dehydrogenation was generally attributed to the electronic and ensemble effects [4]. Despite of no consensus on whether electron rich or deficient Pt is responsible for the high selectivity and stability in propane dehydrogenation, it should be noted that an opposite binding energy changing tendency can be expected if the electronic effect exist between Pt and Sn⁰ or Sn²⁺/Sn⁴⁺ [64,70–72]. However, the shift of Sn⁰ or Sn²⁺/Sn⁴⁺ binding energy on various catalysts follows the order PtSn-B-ZrO₂-11 > PtSn-B-ZrO₂-9 ≈ PtSn-B-ZrO₂-10, suggesting the lowest electron density of Sn⁰ or Sn²⁺/Sn⁴⁺ on PtSn-B-ZrO₂-11. In light of the binding energy variation of Pt and Sn determined from XPS, the influence of support on the electronic property of Pt and Sn cannot be neglected. Although the existence of Pt⁰ and Sn⁰ can be confirmed by the XPS results in this work, the previous XAFS result showed that not all reduced Sn⁰ would form alloy with Pt [73]. An XAFS study also suggested three kinds of platinum species: PtSn alloy, Pt-O-Sn²⁺ species, and pure Pt clusters [74]. The Py-IR result shows that only Lewis acid is present, and the NH₃-TPD result shows that the acidity strength increases linearly with support synthesis pH. It was reported that Lewis acid sites played a decisive role in providing anchoring sites for Pd or Pt and electron deficient Pd or Pt would be obtained due to the interaction between Pd or Pt and Lewis acid sites [26,28,75]. Thus, we can anticipate that Pt or Sn species, especially those separate species directly bound to support, might be electron deficient because of the binding effect of Lewis acid sites, and stronger Lewis acid would lead to more electron deficient Pt⁰ or Sn species, which would show higher binding energy in XPS results [75].

Some studies reported that the structure of PtSn may influence the catalyst stability but it is still not clear yet which kind of PtSn alloy is the best for PDH [64,76–79]. Additionally, the formation of PtSn alloy requires the reduction of SnO_x to Sn⁰ [15]. However, the reduced Sn⁰ was not even detected while good activity and stability were still obtained in some reports [29,80]. In this study, the oxidation state of Sn is mainly Sn²⁺/Sn⁴⁺ as shown in XPS results, in contrary to easier reduction of Sn on ZrO₂ in previous reports [35,36]. This indicates the stronger binding of Sn on boron modified ZrO₂. The better stability obtained on PtSn/B-ZrO₂-10 with less portion of Sn⁰ is in accordance with previous research that an improved stability was obtained on supports which stabilized the oxidized SnO_x [13,35,36,81,82]. Furthermore, it implies that the reduction of SnO_x to form PtSn alloy may not be the prerequisite to improve catalytic performance while the interaction between Pt and Sn may play a more important role in catalyst stability [13,15,83]. It has been pointed out that the interaction between Pt and Sn can also be affected by their respective interaction with support [74,79]. Considering the stronger Lewis acid sites, the less fraction of Pt⁰ and most electron deficient Sn species, stronger interaction between the metal species and the support can be expected on PtSn/B-ZrO₂-11 compared to PtSn/B-ZrO₂-9 and PtSn/B-ZrO₂-10. However, as CO oxidation result shows, the interaction between Pt and Sn on PtSn/B-ZrO₂-11 may be inferior to that on PtSn/B-ZrO₂-10. Accordingly, it can be induced that moderate interaction be-

tween the metal species and the support would intensify the interaction between Pt and Sn, which obviously benefit propane dehydrogenation.

3.2.3. Coking behavior

The general scheme of coke formation on PtSn-based catalysts in PDH can be summarized as follows: first, coke precursor with a high hydrogen to carbon ratio is likely generated on Pt metal during reaction; then the precursor migrates to the support and undergoes oligomerization, cyclization, and condensation into more graphitized carbonaceous deposits with a low H/C [60,84,85]. The coke with higher H/C located on metal or in the vicinity of metal was reported to show a lower oxidation temperature in the range of 250–300 °C, while the coke located on support was oxidized at a higher temperature [85]. It can be seen from the Raman result that coke deposited on PtSn/B-ZrO₂-10 is more hydrogen deficient than that on PtSn/B-ZrO₂-11. However, the main oxidation temperature of coke on PtSn/B-ZrO₂-10 is lower than that on PtSn/B-ZrO₂-11 (Fig. 9). This may be due to the higher OSC on PtSn/B-ZrO₂-10 compared to PtSn/B-ZrO₂-11, as higher oxygen storage capacity would facilitate the oxygen mobility and thus lower oxidation temperature of carbonaceous species on support [56,86,87]. The more intense signal in the range of 250–300 °C on PtSn/B-ZrO₂-9 and PtSn/B-ZrO₂-11 than that of PtSn/B-ZrO₂-10 implies that more coke is deposited on metal for PtSn/B-ZrO₂-9 and PtSn/B-ZrO₂-11. The better stability obtained on PtSn/B-ZrO₂-10 than PtSn/B-ZrO₂-11 might be attributed to less coke deposited on metal.

Additionally, the drain effect of Sn that facilitates the migration of coke precursor from Pt surface is proposed to account for the improved stability after introduction of Sn [10]. Thus, it can be anticipated that more intimate interaction between Pt and Sn exist on PtSn/B-ZrO₂-10 which leads to more dehydrogenated coke migrating to the support and needing a higher combustion temperature, in line with the TPO results.

4. Conclusions

The pH value during preparation of B-ZrO₂-x (x = 9, 10, 11) supports affected the catalytic performance of PtSn/B-ZrO₂-x catalysts in non-oxidative dehydrogenation of propane. The amount and strength of Lewis acid sites on B-ZrO₂ were found to increase with the synthesis pH value of B-ZrO₂. Because no linear relationship between OSC and CO oxidation activity was observed, it is hypothesized that the interaction between Pt and Sn plays a dominant role and increases in the order PtSn/B-ZrO₂-9 < PtSn/B-ZrO₂-11 < PtSn/B-ZrO₂-10. A moderate interaction between the metal species and B-ZrO₂-10 strengthens the interaction between Pt and Sn, and hence facilitates the migration of coke precursor from the active sites to the support, resulting in a better stability in PDH.

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Graphical Abstract

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Effect of pH on the catalytic performance of PtSn/B-ZrO₂ in propane dehydrogenation

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The better stability of the catalyst PtSn/B-ZrO₂ in propane dehydrogenation is likely attributed to a moderate interaction between metal species and the support and hence a strong interaction between Pt and Sn species.

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B修饰的ZrO₂及其制备pH值对PtSn/B-ZrO₂丙烷脱氢反应性能的影响

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摘要: 丙烯作为一种重要的石油化工基础原料, 传统上是从石脑油蒸汽裂解或催化裂化过程中作为副产物生产的。随着原油的枯竭和页岩气开发技术的成熟, 通过乙烷蒸汽裂解制备乙烯更具吸引力并已得到广泛的工业应用, 但该路线乙烯选择性高, 而副产物丙烯数量有限。为满足不断增加的丙烯需求量, 利用油田气和页岩气中低附加值的丙烷为原料, 将其直接脱氢制丙烯(PDH)具有重要的现实意义。目前已开发成功的PDH技术采用的催化剂主要为负载PtSn型催化剂和Cr基催化剂。其中, Pt基催化剂较Cr基催化剂更加环境友好, 因此得到了更广泛的应用。由于Pt元素的昂贵和稀有, 制备低Pt含量和良好性能的催化剂极具吸引力。UOP Oleflex工艺开发的最新一代催化剂DEH-16仅含有0.3 wt% Pt, 相对于前一代催化剂Pt含量降低30%。然而, 许多文献报道, 随着Pt含量的降低, 催化剂的稳定性很容易恶化, 降低Pt含量并保持催化性能仍具

有一定的挑战。研究表明,含有更多Lewis酸性位点和更少Brönsted酸位点的催化剂显示出较好的丙烷脱氢活性和丙烯选择性。此外,源自缺陷位或配位不饱和位的Lewis酸性位点也可作为负载的金属颗粒提供锚定位点。BASF对ZrO₂作为载体的丙烷脱氢催化剂进行了广泛研究,但其催化剂尚未完全商业化。有文献报道,ZrO₂负载的PtSn催化剂在脱氢反应中的稳定性较差。将元素硼(B)加入到ZrO₂中可以极大地抑制Brönsted酸性而提高Lewis酸量和酸强度,因此我们推测含有适量配位不饱和Zr位点的ZrO₂作为PtSn丙烷脱氢催化剂载体可能具有优异的性能。载体的合成pH值对催化剂PDH性能也会有影响。然而,目前还没有硼改性的ZrO₂ (B-ZrO₂)合成pH值对PDH催化性能影响的研究。

本文研究了B-ZrO₂的合成pH值(9, 10和11)对PtSn/B-ZrO₂在丙烷脱氢反应中催化性能的影响。Py-IR结果表明各pH值下合成的B-ZrO₂均只有Lewis酸, NH₃-TPD结果则表明B-ZrO₂的Lewis酸量和强度随合成pH值的增加而增加。XPS结果显示,载体对Pt和Sn电子性质的影响不容忽视。由于OSC与CO氧化活性之间没有线性关系,因此Pt和Sn之间的相互作用程度在CO氧化反应中可能起主要作用,并有如下递增趋势: PtSn/B-ZrO₂-9 < PtSn/B-ZrO₂-11 < PtSn/B-ZrO₂-10。由于PtSn/B-ZrO₂-10中Sn⁰含量适中,适中的被负载金属与载体间的相互作用强度有利于Pt和Sn之间更紧密的相互作用,这可能是该催化剂丙烷脱氢催化活性和稳定性均较好的主要原因。

关键词: 丙烷脱氢; Pt-Sn; 丙烯; 载体; 稳定性

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