

Construction of PtZn/TS-X catalyst mediated by hydroxyl nests and its high-efficiency catalytic performance for propane dehydrogenation

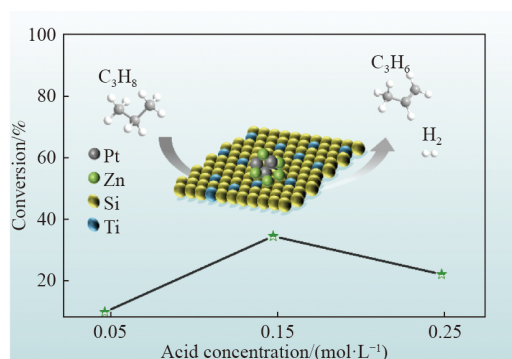
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Abstract: Acid etching enables the enrichment of abundant hydroxyl nests on the surface of titanium silicalite (TS). These hydroxyl nests offer stable anchoring sites for the immobilization of active components, facilitating synergistic interaction with PtZn bimetallic species and enhancing propane dehydrogenation (PDH) catalytic performance. Based on this concept, in the present work, TS supports were etched using hydrochloric acid with varying concentrations, and a series of PtZn/TS bimetallic catalysts were fabricated *via* the co-impregnation method. The effects of acid concentration on the catalyst structure, surface properties, and PDH catalytic performance were systematically investigated.

Comprehensive characterization results reveal that acid etching induces the formation of surface-enriched hydroxyl nest structures on TS supports. These structures act as efficient anchoring centers for PtZn species, leading to enhanced dispersion and increased exposure of metallic Pt⁰ species, thereby lowering the energy barrier for the PDH reaction. This study thus provides a feasible and rational strategy for the design of high-performance PDH catalysts.

Key words: TS zeolite; PtZn bimetal; hydroxyl nest; propane dehydrogenation



Propylene is a key platform chemical for the production of value-added products such as polypropylene and propylene oxide, and its global demand has continued to grow in response to the ongoing upgrading of the chemical industry^[1]. Propane dehydrogenation (PDH) technology has emerged as one of the mainstream propylene production routes, owing to its abundant availability of propane feedstocks and high propylene selectivity^[2]. Pt, characterized by high catalytic for C–H bond activation and low selectivity for C–C bond cleavage^[3–4], is widely regarded as an ideal active component for the PDH reaction. However, under high-temperature reaction conditions, Pt particles are prone to agglomeration, accompanied by severe carbon deposition on the catalyst surface, which together result in a rapid catalyst deactivation^[5]. Therefore, developing a synergistic strategy integrating “additive modification” and “support regulation” is of great

significance for improving the stability and selectivity of Pt-based PDH catalysts^[6].

In PDH reactions, Pt-based catalysts with small particle sizes exhibit significantly higher activity than that of those with large particle sizes^[7–8]. Constructing bimetallic Pt-based catalysts with additive modification is an effective strategy to inhibit the sintering of small Pt species and promote their dispersion^[9–10]. In terms of additive design, Zn has emerged as an efficient modifying additive for Pt-based catalysts, as it can inhibit Pt sintering through geometric hindrance and facilitate the desorption of carbon deposition species *via* electronic effects^[11–14]. However, in most reported Pt-Zn bimetallic systems, research has primarily focused on the catalytic performance of Pt, while Zn has been treated merely as a promoter^[15–17]. For example, Song et al.^[18] demonstrated that upon loading the Pt-Zn bimetallic component onto self-pillared Silicalite-1

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zeolite nanosheets (SP-S-1), the specific surface area of the support was notably enhanced, and abundant Si–OH groups were introduced. This modification substantially augmented the exposure of Pt active sites on the surface of SP-S-1. Similarly, Zhang et al.^[19] reported that Pt-Zn supported on modified ZSM-5 exhibited superior catalytic performance compared to unmodified ZSM-5, where Zn functioned solely as a promoter through geometric and electronic effects.

The synergistic effect between Pt and Zn is highly dependent on the surface structure of the support, which should provide stable anchoring sites for the bimetallic active components to inhibit the agglomeration of PtZn species at elevated temperatures. MFI-type zeolites (e.g. ZSM-5 and S-1), featuring excellent thermal stability and tunable pore structures, are extensively employed as supports for PDH catalysts^[20–22]. Chen et al.^[23] reported the synthesis of Pt-Zn catalysts supported on high-silica HZSM-5, revealing the presence of two distinct types of active sites: Lewis acid sites associated with framework Zn species and small-sized Pt-Zn particles. Another representative MFI-type zeolite, S-1, was investigated by Zhang et al.^[24], who demonstrated that framework-incorporated Zn in S-1 plays a critical role in facilitating and stabilizing PtZn species for efficient PDH performance. This stabilization is attributed to the synergistic effects of spatial confinement imposed on PtZn particles and lattice confinement provided by framework Zn species.

Titanium-silicon zeolite (TS), a prominent member of the MFI-type zeolite family, exhibits exceptional thermal and chemical stability. Framework-incorporated Ti species can modulate the electronic properties of Pt active sites *via* coordination interactions, while surface hydroxyl groups serve as anchoring sites for the immobilization of active components^[25]. Li et al.^[26] reported that PtSn bimetallic nanoparticles supported on TS exhibited the highest PDH activity when the TS particles were small. When employed as a PDH catalyst support, the weak acidity and confined pore environment of TS can effectively suppress side reactions, and the synergistic interaction between framework Ti and metal components significantly enhances the catalyst stability during PDH. However, for the Pt-Zn bimetallic system, strategies to optimize Pt-Zn dispersion by tailoring the surface structure of TS (e.g., hydroxyl nests) and further suppress coking-induced deactivation remain largely unexplored.

Based on these considerations, TS was employed as the support in this study. The surface hydroxyl nest density of TS was regulated *via* acid etching with different concentrations, and a series of PtZn/TS-*X* catalysts were prepared by a co-impregnation method. The influence of acid concentration on the structural evolution of the TS support was systematically investigated. By combining systematic catalytic evaluation with comprehensive structural and spectroscopic characterizations, this work aims to clarify the role of hydroxyl nests in anchoring PtZn species and modulating the structure-performance

relationship in PDH.

1 Experimental

1.1 Catalyst preparation

Commercial TS zeolite (Si/Ti molar ratio=80, Tianjin Yuanli Chemical Co., Ltd.) was employed as the support. Hydrochloric acid (HCl) solutions with concentrations of 0.05, 0.1, 0.15, 0.2 and 0.25 mol/L were prepared separately. For each HCl concentration, the solution was mixed with TS powder at a fixed liquid-to-solid ratio under stirring at 40 °C for 12 h. After etching, the samples were thoroughly washed with deionized water until neutral, followed by drying at 100 °C for 12 h. The dried samples were then calcined at 300 °C with a heating rate of 1 °C/min and maintained for 11 h. The obtained acid-etched supports were denoted as TS-*X*, where *X* represents the concentration of the etching HCl solution in mol/L.

The PtZn/TS-*X* series of catalysts (with a Pt loading of 0.5% and a Zn loading of 2%) were prepared by the co-impregnation method. The specific steps are as follows: A certain amount of hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, analytical grade, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, analytical grade, Tianjin Damao Chemical Reagent Factory) were weighed and dissolved in 20 mL of deionized water. Then, 1 g of TS-*X* was added to the above precursor solution, and stirred at room temperature for 2 h, followed by heating to 50 °C under continuous stirring until complete solvent evaporation. The dried solid was placed in a 100 °C air-circulating oven for 12 h, and then transferred to a muffle furnace and heated at a rate of 1 °C/min to 550 °C, calcined in air for 4 h to obtain the target catalyst, which was denoted as PtZn/TS-*X*. Catalysts with different Zn loadings were prepared following the same procedure.

To explore the individual effects of Pt and Zn, the comparative catalysts 0.5Pt/TS-0.15 and 2Zn/TS-0.15 were prepared during the same metal loading and preparation procedures as those of PtZn/TS-0.15.

1.2 Catalyst characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV diffractometer (Rigaku Corporation, Japan) using Cu *K* α radiation ($\lambda = 1.54 \text{ \AA}$) at an operating voltage of 40 kV and current of 40 mA. The diffraction patterns were recorded over a 2θ range of 5° to 50° with a scanning rate of 2(°)/min. Transmission electron microscopy (TEM) characterization was conducted using a JEOL JEM-F200 microscope (JEOL Ltd., Japan), coupled with an energy-dispersive X-ray spectroscopy (EDS) detector (JED-2300T) for elemental analysis. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) spectra were collected on a Shimadzu UV-3600i Plus spectrometer (Shimadzu Corporation, Japan). Raman

spectra were acquired using a Horiba LabRAM HR Evolution spectrometer (Horiba Ltd., Japan) within a wavenumber range of 50–600 cm^{-1} . Fourier transform infrared spectroscopy (FT-IR) experiments were carried out on a Bruker infrared spectrometer. Prior to measurements, background correction was performed at 500 $^{\circ}\text{C}$ using potassium bromide (KBr) pellets. The catalyst sample was then loaded into an *in situ* reaction cell, pretreated by heating to 500 $^{\circ}\text{C}$ under an argon (Ar) atmosphere for 1 h, and cooled to room temperature. Subsequently, FT-IR spectra were collected at 500 $^{\circ}\text{C}$ under a continuous Ar atmosphere, covering a wavenumber range of 3000–3800 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (United States). The excitation source was a monochromatic Al-K α X-ray, and binding energy values were calibrated against the C 1s peak at 284.8 eV to correct for charge-induced shifts. The dispersion of Pt was quantified *via* CO pulse titration, employing a BSD-Chem C200 temperature-programmed chemisorption analyzer. For hydrogen temperature-programmed desorption (H_2 -TPD) experiments, the procedure was as follows: 100 mg of catalyst was first pretreated by heating to 600 $^{\circ}\text{C}$ for 1 h, followed by reduction in a H_2/N_2 mixture for 1 h. The sample was then cooled to 50 $^{\circ}\text{C}$ to allow complete H_2 adsorption, purged with Ar for 30 min to remove physisorbed species, and subsequently heated from 50 to 650 $^{\circ}\text{C}$ at a ramp rate of 10 $^{\circ}\text{C}/\text{min}$. H_2 desorption signals were detected using a thermal conductivity detector (TCD). Thermogravimetric analysis (TGA) was carried out on a HITACHI STA200 thermogravimetric analyzer (Japan), where samples were heated to 600 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ under an air atmosphere.

1.3 Catalyst evaluation

The activity test of PDH under atmospheric pressure was carried out in a fixed-bed quartz reactor (outer diameter: 8 mm). A 0.1 g of catalyst (40–60 mesh) was diluted with quartz sand and loaded into the quartz tube, where the lower end was packed with quartz wool to immobilize the catalyst bed. Prior to the reaction, the catalyst was reduced in a flowing H_2/Ar mixture (12 mL/min, 10% H_2) at 600 $^{\circ}\text{C}$ for 1 h, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Subsequently, the reaction feed ($\text{C}_3\text{H}_8/\text{Ar} = 4:6$) was introduced into the catalyst bed at a total flow rate of 30 mL/min, and the PDH reaction performance was evaluated isothermally at 600 $^{\circ}\text{C}$. The effluent products were analyzed online in real time using a Hua'ai GC9560 gas chromatograph. The calculations of propane conversion and propylene selectivity were based on the following formulas:

$$x(\%) = \frac{n(\text{C}_3\text{H}_{8\text{in}}) - n(\text{C}_3\text{H}_{8\text{out}})}{n(\text{C}_3\text{H}_{8\text{in}})} \times 100\% \quad (1)$$

$$s(\%) = \frac{n(\text{C}_3\text{H}_6\text{out})}{n(\text{C}_3\text{H}_{8\text{in}}) - n(\text{C}_3\text{H}_{8\text{out}})} \times 100\% \quad (2)$$

where $x(\%)$ and $s(\%)$ denote the propane conversion and propylene selectivity, respectively, while $n(\text{C}_3\text{H}_8)$ and $n(\text{C}_3\text{H}_6)$ represent the molar amounts of propane and propylene. The subscripts “in” and “out” refer to the inlet and outlet streams of the reactor.

2 Results and discussion

2.1 Evaluation of catalyst performance

Figure 1(a) shows the effects of different acid concentrations on PDH performance. Compared with catalysts etched at other acid concentrations, PtZn/TS-0.15 exhibits the best catalytic performance, delivering an initial propane conversion rate of 34.2% and a propylene selectivity of 99.6%. Further increasing the acid concentration leads to a gradual decline in conversion rate and propylene selectivity. Based on these results, PtZn/TS-0.05, PtZn/TS-0.15 and PtZn/TS-0.25 were selected as representative catalysts for stability tests. As shown in Figure 1(b), the conversion rate of PtZn/TS-0.15 remained stable at 21.7% after 15 h, whereas PtZn/TS-0.05 exhibits a much lower initial conversion of only 9.5%. The deactivation parameters summarized in Table 1 indicate that catalyst stability follows the order: PtZn/TS-0.15 > PtZn/TS-0.25 > PtZn/TS-0.05. Overall, PtZn/TS-0.15 combines high initial activity and selectivity with a relatively low deactivation rate, demonstrating its favorable performance under the tested conditions. Table 2 further compares the PDH performance of PtZn-based catalysts reported in the literature. Notably, although the propane conversion of PtZn/TS-0.15 is moderate, its propylene selectivity is higher than that of most previously reported catalysts.

Figure 2(a) shows the effect of Zn loading on the PDH performance of PtZn/TS-0.15 catalysts. Propane conversion initially increases and then decreases with increasing Zn content, reaching a maximum of 34.2% at 2% Zn, which is significantly higher than the other loadings (0, 4% and 6%). Propylene selectivity remains above 95% for all Zn loadings, with a maximum of 99.6% at 2% Zn. The optimal performance at 2% Zn may be attributed to the most effective interaction between PtZn species and the TS support, facilitating propane activation^[27]. Figure 2(b) presents the Arrhenius plots ($\ln r$ versus $1/T$) for 0.5Pt2Zn/TS-0.15, 0.5Pt/TS-0.15 and 2Zn/TS-0.15 catalysts at reaction temperatures of 540, 555, 570, 585 and 600 $^{\circ}\text{C}$. Compared with the monometallic Pt/TS-0.15 and Zn/TS-0.15 catalysts, PtZn/TS-0.15 exhibits a significantly lower activation energy, indicating that the efficient synergy between Pt, Zn and the support reduces the reaction energy barrier and enhances catalytic activity.

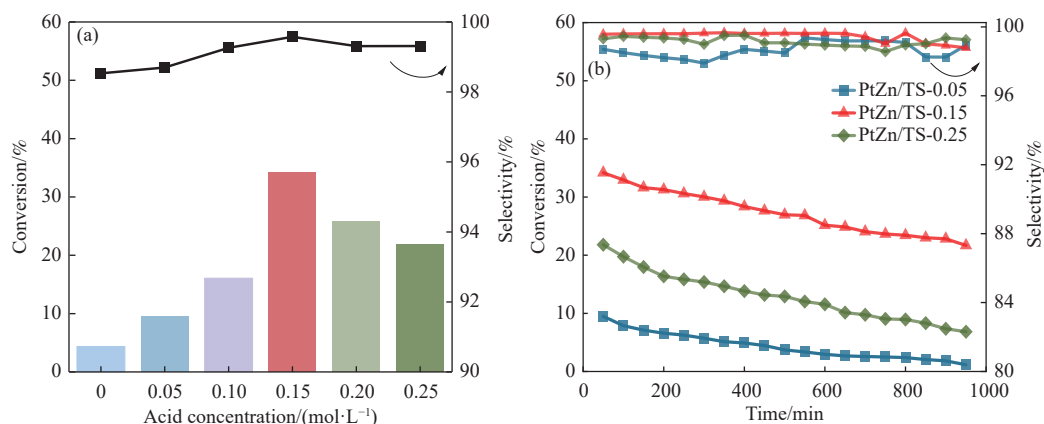


Fig. 1 Performance of PtZn/TS-X for PDH at different acid concentrations: (a) Activity test, (b) Stability test (atmospheric pressure, 600 °C, C₃H₈:Ar=4:6, WHSV=12 h⁻¹)

Table 1 Initial conversions (x_a), final conversions (x_b), deactivation parameters (d), and initial selectivity (s_a) of samples

Sample	$x_a/\%$	$x_b/\%$	d	$s_a/\%$
PtZn/TS	4.4	0	—	98.5
PtZn/TS-0.05	9.5	1.2	87.4	98.7
PtZn/TS-0.15	34.2	21.7	36.5	99.6
PtZn/TS-0.25	21.8	6.8	68.8	99.3

$$d=100\% \times (x_a - x_b/x_a).$$

Table 2 Comparison of performance data of Pt-based catalysts used in the PDH reaction

Catalyst	$t/^\circ\text{C}$	Feed composition	$x_a/\%$	$s_a/\%$	WHSV/h ⁻¹	Active site	Reference
Pt/Zn-MSN	590	C ₃ H ₈ :N ₂ =1:2	51.3	98.7	4.7	Pt	[27]
ZnPt/HZSM-5	525	C ₃ H ₈ :N ₂ =1:19	43.0	93.0	2	Pt-Zn synergism	[23]
PtZn/SiO ₂	600	C ₃ H ₈ :H ₂ =1:1	48.5	96.0	4	PtZn ₄	[28]
PtZn@S-1-Fin	600	Pure C ₃ H ₈	48.3	97.1	12	Pt-Zn clusters	[29]
PtZn@S-1	600	C ₃ H ₈ :H ₂ :N ₂ =1:1:2	46.6	99.0	5.9	Pt-Zn alloy	[24]
PtZn/SP-S-1	580	Pure C ₃ H ₈	40.0	98.5	15	Pt	[18]
PtZn@S-1	550	C ₃ H ₈ :N ₂ =11:19	45.3	99.0	6.5	PtZn clusters	[30]
PtZnALD/SiO ₂	600	C ₃ H ₈ :He=1:4	53.0	97.0	23.6	Pt ₁ Zn ₁	[31]
PtZnO/Al ₂ O ₃	600	C ₃ H ₈ :H ₂ =1:1	35.0	97.0	3	Zn ²⁺	[32]
Pt-Zn/TS-0.15	600	C ₃ H ₈ :Ar=4:6	34.2	99.6	12	Pt	this work

x_a : Initial conversion (%); s_a : Initial selectivity (%).

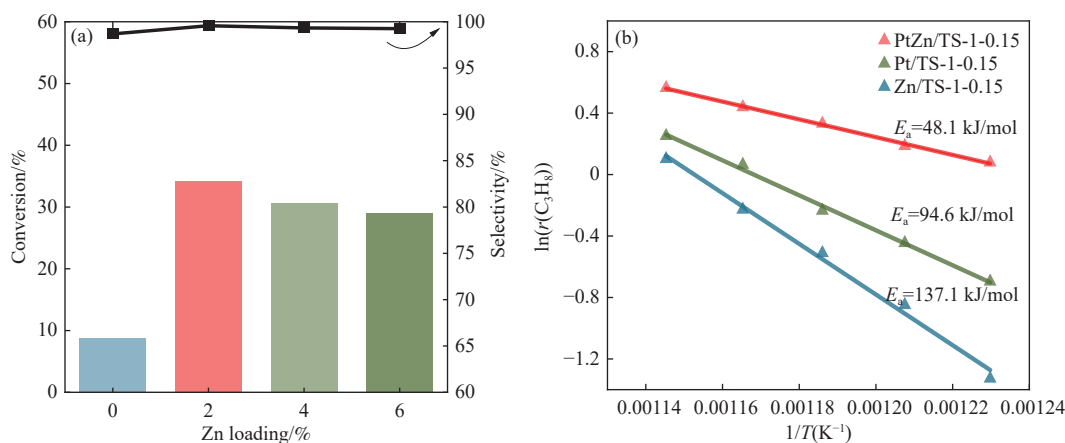


Fig. 2 PDH performance: (a) different Zn loading, (b) Arrhenius curves of PtZn/TS-0.15, Pt/TS-0.15 and Zn/TS-0.15 (C₃H₈:Ar =4:6, WHSV=12 h⁻¹)

2.2 Catalyst characterization

The effects of different HCl etching concentration on the structure on the PtZn/TS-*X* catalysts were investigated through a series of characterization techniques. Figure 3 shows XRD patterns of PtZn/TS-*X* catalysts with different concentrations of HCl. As shown in the figure, the five characteristic diffraction peaks at $2\theta=7.92^\circ$, 9.96° , 23.26° , 24.03° and 24.63° in all catalyst samples are associated with the “five-finger peaks” of the MFI topology^[33–35]. The introduction of PtZn and etching at different acid concentrations did not alter the MFI structure of TS. No characteristic diffraction peaks of PtZn were detected in any catalyst, indicating that PtZn are highly dispersed on the TS zeolite support without noticeable agglomeration or crystallization.

TEM characterization of the PtZn/TS-0.15 catalyst was conducted to examine the morphology and dispersion of metal species. As shown in Figure 4, the Pt-based particles are uniformly dispersed without obvious agglomeration. The lattice spacing of 0.36 nm corresponds to the (101) crystal plane of the anatase type TiO_2 , where electrons are confined to the Ti5c site on the surface and are in a shallow capture state, facilitating electron migration^[36].

In addition, to further investigate the microstructure, energy dispersive X-ray elemental spectroscopy (EDS) characterization was performed on the PtZn/TS-0.15 catalyst. As shown in Figure 5, PtZn elements were uniformly distributed, indicating that PtZn was successfully loaded in the sample.

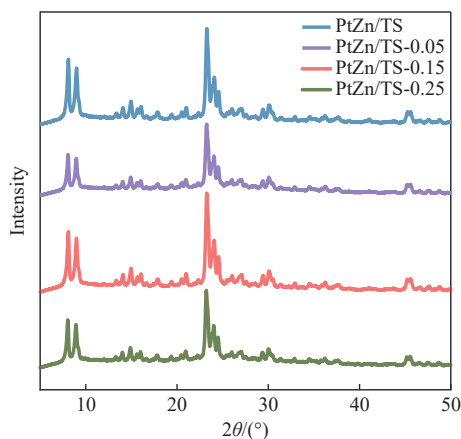


Fig. 3 XRD patterns of PtZn/TS-*X* catalysts

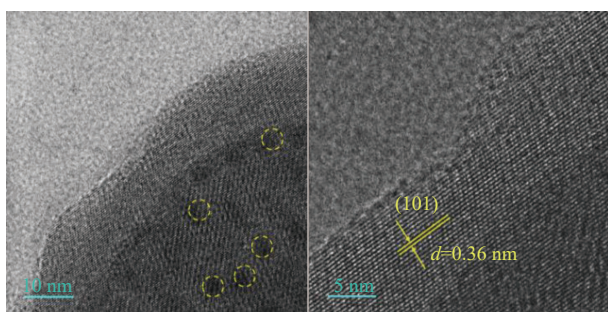


Fig. 4 TEM images of the PtZn/TS-0.15 catalyst

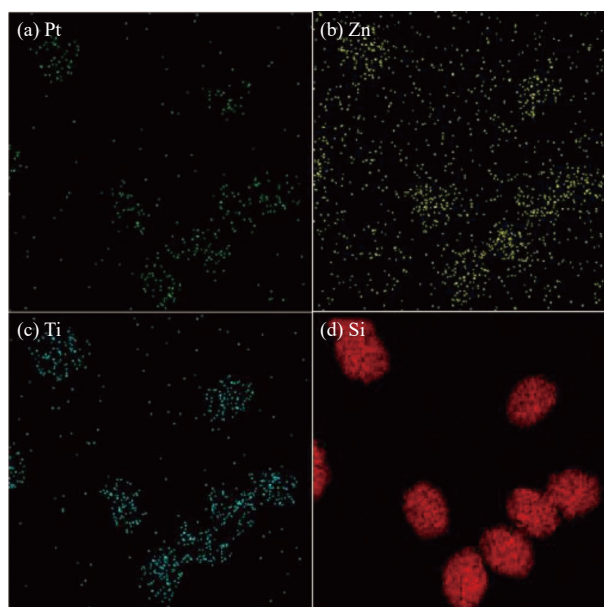


Fig. 5 EDS element mapping diagrams of PtZn/TS-0.15 catalyst

To further verify the effect of acid etching on the evolution of Ti species, ultraviolet-visible diffuse reflectance spectroscopy was used to investigate the coordination state of Ti in PtZn/TS-*X* catalysts. The spectra are shown in Figure 6. According to previous reports^[37], the strong absorption peaks of the samples at 200 and 270 nm belong to framework four-coordinated Ti and extra-framework six-coordinated Ti respectively, while the absorption peak at 330 nm is the characteristic absorption peak of anatase TiO_2 ^[38–39]. It can be seen from the spectra that the intensity of the characteristic absorption peak of Ti^{4+} at 200 nm of the catalyst after acid etching is weakened, and the absorption peak shifts towards the longer wavelengths, indicating the transformation of the four-coordinated Ti to the high-coordinated Ti species. This process is likely associated with the partial cleavage of Ti–O bonds, leading to the detachment of framework Ti and the formation of extra-framework Ti species.

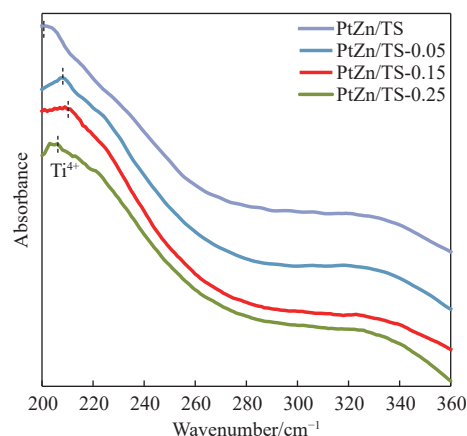


Fig. 6 UV-vis diffuse reflectance spectra of PtZn/TS-*X* catalysts

Among them, PtZn/TS-0.15 exhibits the most pronounced shift of the Ti coordination-related absorption band, suggesting to the greatest degree of Ti–O bond disruption. Further increasing the acid etching severity results in a continuous increase in free Ti species, which can interact with hydroxyl groups to form hydroxylated Ti species. Subsequent condensation of these hydroxylated Ti species leads to the formation of Ti–O–Ti structures, which may partially cover the originally exposed hydroxyl nest sites.

Raman spectroscopy is widely used to probe atomic vibrations in zeolites^[40]. As shown in Figure 7, the characteristic peak at 150 cm^{−1} belongs to the vibration of the Ti–O bond^[41], the peak at 385 cm^{−1} belongs to the vibration signal of platinum oxide^[42], and the absorption peak near 515 cm^{−1} belongs to the vibration absorption of anatase^[43]. For the PtZn/TS-0.15 catalyst, the extensive cleavage of Ti–O bonds results in a reduced vibrational frequency of the Ti–O linkage, leading to a noticeable red shift of the ~150 cm^{−1} band. This observation further confirms the process of the transformation from skeleton Ti to extra-framework Ti. When the acid concentration was increased to 0.25 mol/L, hydroxylated Ti condensed to form the Ti–O–Ti (Ti–O) bond structure, which increased the vibration frequency of Ti–O bonds. Consequently, a blue shift at 150 cm^{−1} was observed. This phenomenon is consistent with the evolution of the Ti coordination environment inferred from ultraviolet-visible spectra.

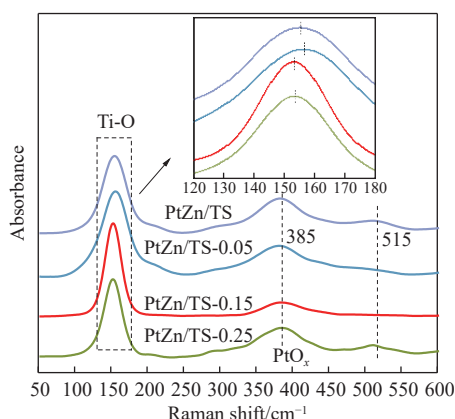


Fig. 7 Raman spectra of PtZn/TS-*X* catalysts after reduction

To deeply explore the types and distribution characteristics of hydroxyl groups on the surface of TS support, FT-IR was used to characterize the hydroxyl vibration of TS-*X* samples. As shown in Figure 8, there are two characteristic absorption peaks in the hydroxyl vibration region, located at approximately 3710 and 3500 cm^{−1} respectively, belonging to the isolated hydroxyl and hydroxyl nest on the TS-*X* surface^[44]. By comparison, it was found that the area of the characteristic peak of the hydroxyl nest of the TS-0.15 at 3500 cm^{−1} was significantly larger than that of the other samples, indicating a significantly higher abundance of hydroxyl nests. In contrast, when the acid concentration increased to 0.25 mol/L, the hydroxyl

content decreased. Combined with the aforementioned UV-vis and Raman results, this behavior can be rationalized by the excessive generation of free Ti species at higher acid etching severity. These free Ti preferentially interact with hydroxyl nest sites to form hydroxylated Ti species, which subsequently undergo condensation reactions to generate Ti–O–Ti (Ti–O) bond structure. As a result, the originally exposed hydroxyl nest active sites are progressively covered, leading to a pronounced reduction in detectable hydroxyl groups. These results indicate that the concentration of hydroxyl nests does not monotonically increase with the increase of acid etching concentration.

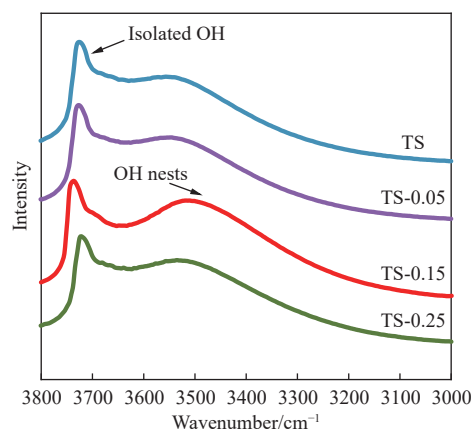


Fig. 8 FT-IR spectra on hydroxyl groups of TS-*X*

Figure 9 further compared the evolution of hydroxyl nests of on TS-*X* support before and after PtZn loading. As shown in Figure 9(a)–(d), the intensity of the characteristic peak corresponding to the isolated hydroxyl group at 3720 cm^{−1} remains nearly unchanged after metal loading, indicating that PtZn species do not significantly interact with the isolated hydroxyls. In contrast, the intensity of the strong absorption band corresponding to the hydroxyl nest at 3500 cm^{−1} is markedly attenuated upon PtZn incorporation. This phenomenon indicates that following the introduction of metal components, most hydroxyl nest sites on the TS support are occupied by the introduced metal species, leading to a reduction in the number of hydroxyl nests and a significant decrease in band intensity^[45–46]. Among the acid-etched samples, PtZn/TS-0.15 exhibits the largest decrease in hydroxyl-nest intensity, indicating the strongest interaction between the PtZn bimetallic and TS support treated with 0.15 mol/L HCl. This result demonstrates that the hydroxyl nests serve as effective anchoring sites for PtZn species, consistent with literature reports highlighting their role in stabilizing metal species^[18]. Accordingly, PtZn/TS-0.15 catalyst exhibits optimal PDH performance, which is associated with the formation of stable and highly active metal species on the TS-0.15 support. The Pt dispersion data summarized in Table 3 further support this conclusion. Pt dispersion in PtZn/TS-0.15 is 23.2%, and as the acid concentration increases further, the corresponding Pt dispersion drops to 19.5%, which is lower than that of PtZn/TS-0.15. Combined with FT-IR results, it is known that the dispersion of Pt is

closely related to the abundance of hydroxyl nests on the support. An enriched hydroxyl-nest environment provides

effective anchoring sites, thereby promoting the dispersion and stabilization of Pt species.

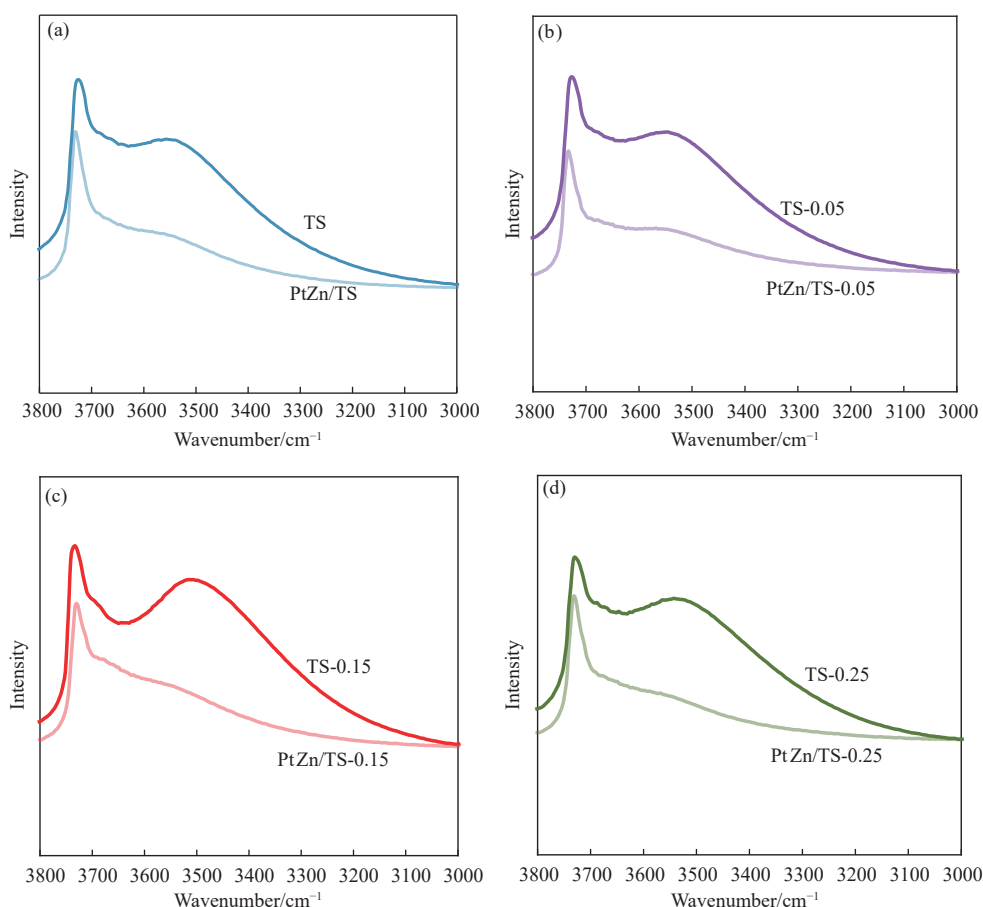


Fig. 9 FT-IR spectra on hydroxyl groups of the TS-X and PtZn/TS-X

Table 3 The distribution and dispersion degree of Pt species in the PtZn/TS-X after reduction

Sample	$\text{Pt}^0/(\text{Pt}^0 + \text{Pt}^{2+})/\%$	$\text{Pt}^{2+}/(\text{Pt}^0 + \text{Pt}^{2+})/\%$	Dispersion degree of Pt/%
PtZn/TS	91.4	8.6	10.3
PtZn/TS-0.05	92.5	7.5	15.8
PtZn/TS-0.15	96.5	3.5	23.2
PtZn/TS-0.25	93.7	6.3	19.5

XPS analysis was employed to elucidate the chemical states of Pt species in the PtZn/TS-X catalysts, as shown in Figure 10. The Pt 4f spectra can be deconvoluted into two sets of doublets, corresponding to metallic Pt^0 and oxidized Pt^{2+} species. Specifically, the $4f_{7/2}$ and $4f_{5/2}$ binding energies of Pt^0 are approximately 72.0 and 75.5 eV respectively, and the $4f_{7/2}$ and $4f_{5/2}$ binding energies of Pt^{2+} are approximately 73.1 and 76.4 eV respectively^[47–49]. According to previous studies^[50–51], Pt^0 is generally regarded as the main active center for PDH and a higher fraction of Pt^0 is beneficial for PDH activity. The relative proportions of Pt^0 and Pt^{2+} species, summarized in Table 3, show clear differences among the catalysts. The proportions of Pt^0 species in PtZn/TS, PtZn/TS-0.05, PtZn/TS-0.15 and PtZn/TS-0.25 are 91.4%, 92.5%, 96.5% and 93.7%, respectively. Notably, PtZn/TS-0.15 exhibits the highest proportion of Pt^0 species,

indicating that metallic Pt is the dominant surface species on this catalyst. This result is well consistent with the FT-IR analysis, which demonstrates that the TS-0.15 support is enriched with hydroxyl nests. These hydroxyl nests act as effective anchoring sites for Pt species, facilitating their uniform dispersion and stabilizing Pt in the metallic state, thereby increasing the surface exposure of active Pt^0 species.

To further investigate the regulation mechanism of acid etching on the PtZn/TS-X catalyst, the H_2 adsorption capacity of the catalyst was determined using H_2 -TPD, as shown in Figure 11. All catalysts showed two desorption peaks, among which the low-temperature desorption peak (~150 °C) was attributed to the H_2 desorbed from metallic Pt, and the high-temperature desorption peak (300–450 °C) was attributed to hydrogen spillover from Pt to the support hydrogen overflow^[52–55]. According to the literature

reports^[56–58], abundant spillover hydrogen is beneficial for suppressing carbon deposits and thereby improving catalyst stability during PDH. Among the catalysts, PtZn/TS-0.15 has the largest H₂ desorption peak in the high-temperature range, indicating the largest H₂ desorption capacity and the strongest hydrogen spillover effect. This behavior suggests enhanced exposure of metallic Pt⁰ species, which can be attributed to the optimal interaction between PtZn species and the acid-etched TS-0.15 support^[59]. The essence of this phenomenon is that surface hydroxyl groups act as anchoring sites for PtZn species, thereby effectively increasing the exposure of Pt⁰ on the support.

Carbon deposition is a major cause of deactivation of Pt-based catalysts. TG characterization was employed to evaluate carbon deposition on the used catalyst. Figure 12 shows the TG profile of PtZn/TS-0.15 after 15 h of PDH reaction. Two distinct weight-loss regions can be observed. The first weight loss below 300 °C is attributed to the removal of adsorbed water and residual surface species. The second weight loss occurring between 300 and 600 °C corresponds to the combustion of carbonaceous deposits, amounting to 1.18%. The relatively low level of carbon deposition contributes to the improved stability of the catalyst.

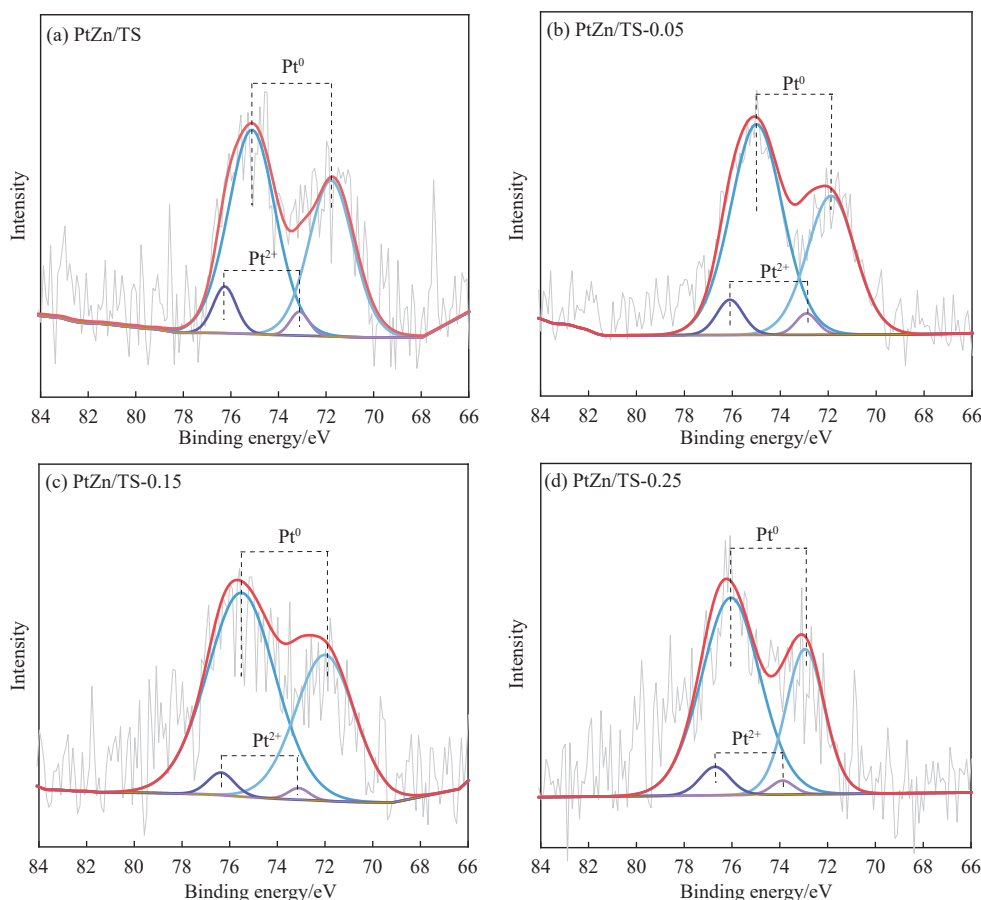


Fig. 10 Pt 4f orbital XPS spectra of the PtZn/TS-*X* after reduction

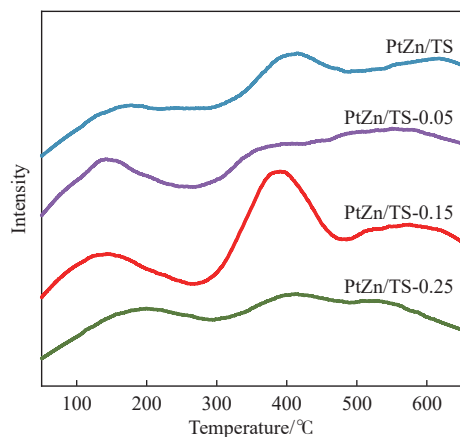


Fig. 11 H₂-TPD profiles of PtZn/TS-*X* catalysts

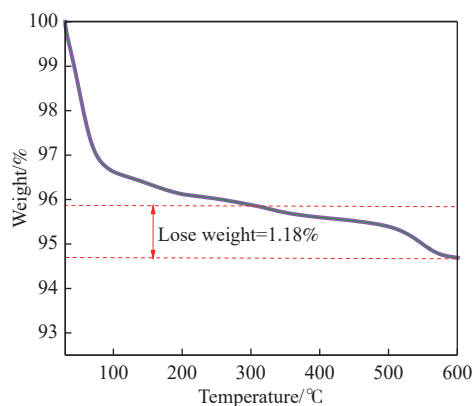


Fig. 12 TG curve of the spent PtZn/TS-0.15

Figure 13 shows the XRD pattern of PtZn/TS-0.15 after the reaction. The catalyst still retains the characteristic diffraction peaks of the TS zeolite, with no obvious changes in peak position or intensity, indicating the has excellent structural stability of the TS framework under high-temperature PDH conditions. In addition, no distinct carbon species-characteristic diffraction peaks were detected, indicating a low level of carbon deposition on the catalyst surface. This observation is consistent with the TG characterization results.

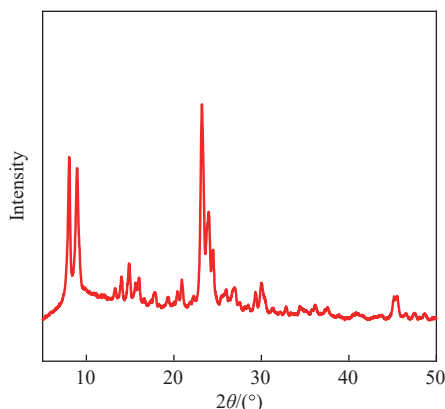


Fig. 13 XRD patterns of the spent PtZn/TS-0.15

3 Conclusions

In this paper, a series of PtZn/TS-*X* bimetallic catalysts were prepared by regulating the surface structure of TS supports *via* acid etching, and the relationship between catalyst structure and PDH performance was systematically investigated. Under reaction conditions of 600 °C and WHSV=12 h⁻¹, the initial conversion rate reached 34.2%, with propylene selectivity up to 99.6%. After 15 h of continuous reaction, the conversion rate remained 21.7%, the deactivation parameter was as low as 36.5%, and the carbon deposit on the catalyst surface was only 1.18%. The excellent performance of PtZn/TS-0.15 is attributed to acid etching induced formation of enriched hydroxyl nests on the TS surface. These hydroxyl nests provide efficient anchoring sites for PtZn species, promoting high dispersion and increasing the surface exposure of Pt⁰ to 96.5%, thereby generating abundant highly active sites for the PDH. In addition, the synergistic interaction between hydroxyl nests and PtZn significantly lowers the reaction energy barrier, enhancing both activity and stability. This study not only enriches the preparation and modification methods of zeolite-based catalytic materials, but also provides important theoretical guidance for the efficient catalytic conversion of light alkanes.

Declaration of Competing Interest

The authors declare no conflict of interest.

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羟基巢介导的 PtZn/TS-X 催化剂构建及其高效催化丙烷脱氢

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摘 要: 酸刻蚀可以使钛硅分子筛(TS)表面富集大量羟基巢, 与 PtZn 金属协同提升丙烷脱氢(PDH)反应的催化性能, 同时为活性组分的负载提供稳定的锚定位点。基于此, 本工作通过不同盐酸浓度刻蚀 TS 载体, 并采用共浸渍法制备 PtZn/TS 系列双金属催化剂, 研究了酸浓度对催化剂结构、表面性质及 PDH 反应性能的影响规律。结合 XRD、EDS、Raman、UV-vis、FT-IR、XPS、H₂-TPD、TG 等表征分析表明, 酸刻蚀使 TS 载体表面形成富集的羟基巢结构, 该羟基巢能作为 PtZn 的高效锚定位点, 显著提升 Pt⁰ 暴露程度, 同时降低 PDH 反应能垒。本研究为设计高效 PDH 反应催化剂提供了可行思路。

关键词: 钛硅分子筛; PtZn 双金属; 羟基巢; 丙烷脱氢

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