

Influence of hydroxyl nest structure of all-silicon supports on efficient propane dehydrogenation over PtZn catalysts

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Abstract

To investigate the effect of hydroxyl nest structure on the performance of PtZn bimetallic catalysts for propane dehydrogenation (PDH), four all-silica materials, namely S-1, S- β , MCM-41 and SBA-15, were selected as supports and a series of catalysts were constructed by co-impregnation loading PtZn bimetallic catalysts. Catalyst structures were characterized by means of XRD, N₂ adsorption-desorption, FT-IR, XPS, etc. The characterization results indicated that the PtZn/S-1 catalyst had the highest content of hydroxyl nests, and the abundant hydroxyl groups on the support surface could provide stable anchoring sites for the PtZn active component, significantly increasing the exposure of Pt⁰. The activity test results showed that the PtZn/S-1 catalyst exhibited optimal catalytic performance under reaction conditions of 600°C and WHSV=13.39 h⁻¹: propane conversion of 29.1%, propylene selectivity of 96.8%, and initial propylene generation rate of 0.79 mmol/g⁻¹·min⁻¹. The study shows that the hydroxyl nest structure of the all-silicon support is a key factor in regulating the dispersion and exposure of the PtZn active center, and provides theoretical support for the structural design of highly efficient PDH catalysts.

Keywords: Hydroxyl nests; Propane dehydrogenation; All-silicon support; PtZn bimetallic

Introduction

Propylene is the second most important petrochemical raw material^{1,2} after ethylene and an extremely important intermediate chemical³. In recent years, its consumer market has remained active and is widely used in the production⁴⁻⁶ of chemicals such as polypropylene and propylene oxide, leading to a continuous increase^{7,8} in the average annual growth rate of national demand for propylene. However, the production of propylene from the traditional naphtha cracking process is limited by the raw material structure and has been unable to meet the growing market demand^{9,10}. Propane dehydrogenation(PDH) technology has become one of the mainstream pathways for propylene production due to its wide availability of feedstock and high selectivity of propylene. Pt, with its high activity for propane C-H bond cleavage and low selectivity for C-C bond splitting^{11,12}, can efficiently activate propane and inhibit deep splitting, making it the preferred active component for the PDH reaction^{13,14}. However, the high-temperature reaction conditions of PDH are prone to causing Pt particle agglomeration and surface carbon, resulting in rapid degradation of activity. Introducing an

additive to construct a bimetallic system is an effective strategy to address this problem^{15,16}. Zn, with its unique properties, becomes an efficient additive for Pt-based catalysts^{17,18}: on the one hand, it hinders the migration and aggregation of Pt atoms through the geometric steric hindrance effect, maintaining its small size advantage. On the other hand, it regulates the Pt electron structure through electron interaction, reducing the adsorption strength of carbon deposit precursors to alleviate carbon deposit deactivation. PtZn bimetallic synergistically optimizes the surface electronic environment and active site distribution, maintains high propane conversion and propylene selectivity, and enhances the catalytic performance of the PDH reaction.

The synergy between Pt and Zn is highly dependent on the surface structure of the support, which needs to provide stable anchoring sites¹⁹ for the bimetallic active components to prevent Pt-Zn particle agglomeration at high temperatures. All-silica supports, which have the advantages of high chemical inertness, no heteroatom interference and excellent thermal stability, can minimize the non-specific interaction between the support and the active metal to the greatest extent and precisely highlight the intrinsic catalytic performance of the bimetallic active center. Therefore, they are the ideal choice for supporting PtZn catalyst supports.

S-1, as a typical MFI type all-silica molecular sieve, has a framework composed only of regularly connected silicon-oxygen tetrahedrons without heteroatom doping^{20,21}. This structure gives it both high chemical inertness and excellent thermal stability. The presence of weakly acidic sites in S-1 is more conducive to the yield of propylene, thereby enhancing the selectivity of the reaction²². Liu et al.²³ used a simple impregnation method to load bimetallic PtZn catalysts on multiple supports, including commercial S-1 zeolite, conventionally synthesized S-1 zeolite, self-supported S-1 zeolite, and amorphous SiO₂. The results showed that the PtZn bimetallic catalysts supported on SP-S-1 exhibited the best catalytic performance, with smaller grain size and faster mass transfer and diffusion rates. Lu et al.²⁴ introduced Pt into multiporous ZnS-1 molecular sieves to produce Pt/Zn-S-1 catalysts. Gao et al.²⁵ synthesized PtZn bimetallic catalysts on nanomaterials (amorphous SiO₂, mesoporous SBA-15, microporous S-1, and mesoporous MCM-41) with abundant weakly acidic sites, and MCM-41 stood out for its unique advantages, including: Large specific surface area, well-distributed pore diameters, and an appropriate number and intensity of acidic sites. It can be seen that many studies have focused on the pore structure of the support or the dispersion of the metal, but there is still a research gap in directional regulation of the electronic state and stability of the metal active center by the hydroxyl nest structure on the

84 surface of the all-silica support. The crystal structure of all-silica supports directly affects the
 85 form of presence of surface hydroxyl groups, where the formation of hydroxyl nest structures
 86 is closely related to topological defects in microporous crystals.

87 To systematically investigate the regulatory effect of the support structure on the
 88 bimetallic active center of PtZn, four all-silica materials with typical structural differences
 89 were selected in this study: Microporous crystal type S-1 (MFI topology), microporous crystal
 90 type S- β (BEA topology), mesoporous amorphous MCM-41 and mesoporous amorphous
 91 SBA-15 were used to prepare a series of PtZn/all-silica catalysts by co-impregnation,
 92 combined with various characterization techniques and catalytic performance tests To
 93 systematically investigate the regulation mechanism of the hydroxyl nest structure of different
 94 all-silica supports on the dispersion of the active center of PtZn, electronic state and PDH
 95 catalytic performance, to reveal the structure-activity relationship between the hydroxyl nest
 96 structure and catalytic performance, and to provide precise theoretical support and
 97 experimental evidence for the directional design of efficient PtZn-based PDH catalysts.

100 Experimental

102 *Catalyst Preparation*

104 A series of bimetallic catalysts with PtZn loaded on different all-silica supports were
 105 prepared by co-impregnation, with the theoretical loading of Pt fixed at 0.5wt% and the
 106 theoretical loading of Zn fixed at 2wt%. The specific steps are as follows: Weigh a certain
 107 amount of chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and zinc nitrate hexahydrate
 108 ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), dissolve them together in 20 mL of deionized water, and stir magnetically
 109 until completely dissolved to prepare a mixed solution of metal precursors. Weigh 1g of
 110 commercial S-1, S- β , MCM-41 and SBA-15 molecular sieve support powder respectively,
 111 add them to the above precursor solutions, stir at room temperature for 2 hours, then heat to
 112 50°C and continue stirring until the liquid is completely evaporated. The evaporated solids
 113 were dried in a 100°C forced convection oven for 12 hours, then transferred to a muffle
 114 furnace and calcined in an air atmosphere at a heating rate of 1°C/min to 550°C for 4 hours.
 115 After natural cooling, the target catalysts were obtained, denoted as PtZn/S-1, PtZn/S- β ,
 116 PtZn/MCM-41 and PtZn/SBA-15.

118 *Catalyst Characterization*

119

120 The Rigaku Ultima IV XRD from Japan was adopted. Cu K α was used as the radiation
 121 source ($\lambda=1.54 \text{ \AA}$), the tube pressure was 40 kV, the tube current was 40 mA, the scanning
 122 range was $2\theta=5^\circ\text{-}50^\circ$, and the scanning rate was $2^\circ/\text{min}$. The microscopic morphology and
 123 structure of the catalyst samples were measured by scanning electron microscopy (SEM)
 124 instruments, using the German ZEISS Sigma 360 field emission scanning electron
 125 microscope. The specific surface area and pore characteristics of the catalyst samples were
 126 characterized by N₂ physical adsorption-desorption experiments using a 4-station fully
 127 automatic specific surface area analyzer of the American Micromeritics APSP 2460 model.
 128 The analysis and calculation were based on the Brunauer-Emmett-Teller (BET) model to
 129 obtain the data of specific surface area, pore volume and pore size of the sample. In-situ FT-
 130 IR was performed on a Bruker infrared spectrometer with a wavenumber of $3000\text{-}3900\text{cm}^{-1}$.
 131 Before the experiment, the background was corrected with KBr at 500°C . After cooling to
 132 room temperature, the catalyst sample was loaded into the in-situ reaction cell. Pre-treatment
 133 was carried out by heating to 500°C in an Ar atmosphere and holding for 1 hour, and the in-
 134 situ infrared spectra of the catalyst were collected at the same temperature and in an argon
 135 atmosphere. H₂-TPR characterization of the samples was performed to analyze the differences
 136 in catalyst reduction temperatures. 0.1g of the sample was placed in a U-tube and pre-treated
 137 with argon(Ar) at 600°C for 1 hour before testing. Then it was cooled to room temperature
 138 and held for 30 minutes, followed by reduction treatment of the sample at 700°C at a rate of
 139 $10^\circ\text{C}/\text{min}$ in an H₂/N₂ (10vol.%H₂) atmosphere. X-ray photoelectron spectroscopy (XPS) was
 140 analyzed on the Thermo Scientific K-Alpha X-ray photoelectron spectrometer in the United
 141 States, using a single Al-K α as the excitation source, and the signal of C1s appearing at 284.8
 142 eV was used to calibrate the binding energy shift produced by the charge effect.
 143 Thermogravimetric analysis was performed on a Hitachi STA200 (Japan) thermogravimetric
 144 analyzer, heated to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere.

145

146 *Catalyst Evaluation*

147

148 PDH atmospheric pressure reactivity test on a fixed-bed quartz reactor. Take 0.1g of
 149 the catalyst (40-60 mesh) and mix it with quartz sand and place it in a quartz tube. Insert
 150 quartz cotton at the lower end to fix the catalyst. Introduce H₂/Ar (12mL/min, 10% H₂
 151 content) and reduce at 600°C for 1 hour at a heating rate of $10^\circ\text{C}/\text{min}$. The reaction mixture

with a total flow rate of 30mL/min ($C_3H_8/Ar=4:6$) was introduced into the catalyst bed and the PDH reaction performance was tested at 600°C. The product was analyzed and detected in real time online using a GC9560 gas chromatograph equipped with an FID detector. The propane conversion and propylene selectivity formulas are as follows:

$$X(\%)=[n(C_3H_8 \text{ in})-n(C_3H_8 \text{ out})]/n(C_3H_8 \text{ in})\times 100\%$$

$$S(\%)=n(C_3H_6 \text{ out})/[n(C_3H_8 \text{ in})-n(C_3H_8 \text{ out})]\times 100\%$$

Where $X(\%)$ and $S(\%)$ represent propane conversion and propylene selectivity respectively, $n(C_3H_8)$ and $n(C_3H_6)$ represent moles of propane and propylene respectively, and the subscripts “in” and “out” represent inlet gas and outlet gas of the reactor respectively. In this experiment, carbon balance > 96%.

Results and discussion

Catalyst Characterization

XRD characterization of PtZn/S-1, PtZn/S- β , PtZn/MCM-41 and PtZn/SBA-15 catalysts was performed to explore the crystal structure of different all-silica supports. As shown in Figure 1, the PtZn/S-1 catalyst presented five characteristic diffraction peaks at $2\theta=7.92^\circ$, 9.96° , 23.26° , 24.03° and 24.63° , all of which were associated with the five typical peaks specific to the MFI topology²⁶, and the PtZn/S- β molecular sieve support still maintained its microporous crystal structure. The PtZn/S-1 and PtZn/S- β molecular sieves were not damaged by PtZn loading, and no characteristic crystal phase diffraction peaks of Pt and Zn were observed, indicating good dispersion of Pt and Zn species on the S-1 and S- β supports. Both PtZn/SBA-15 and PtZn/MCM-41 exhibit characteristic wide peaks at $2\theta\approx 19^\circ$, which are typical amorphous diffraction characteristic peaks. The crystalline structure of PtZn/S-1 provides a structural basis for the formation of hydroxyl nests, while the amorphous supports (MCM-41, SBA-15) have difficulty forming stable hydroxyl nests due to the disordered arrangement of silicon-oxygen tetrahedra.

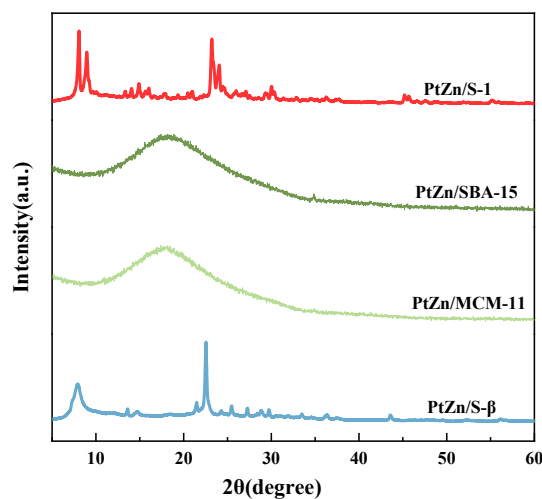


Fig. 1. XRD diffraction patterns of different all-silicon support catalysts.

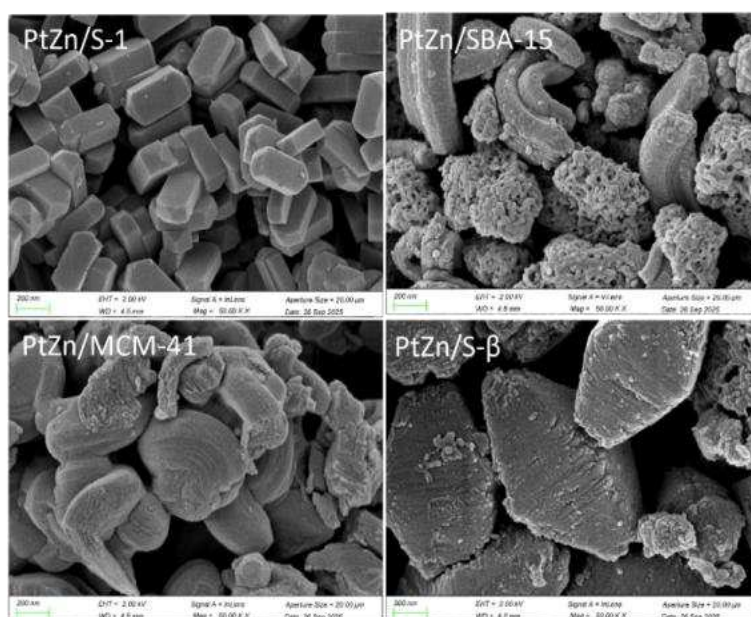


Fig. 2. SEM images of different all-silicon support catalysts.

SEM characterization further revealed morphological differences among different all-silica supports. As shown in Figure 2, PtZn/S-1 presents a regular square columnar packing morphology with smooth and flat crystal planes. This regular crystal plane structure contributes to the uniform dispersion of the active component PtZn on the support surface. The PtZn/S- β molecular sieve retains a distinct crystal angular morphology. In contrast,

PtZn/SBA-15 and PtZn/MCM-41 exhibit amorphous agglomerated structures with rough and irregular surfaces, which are typical characteristics of mesoporous amorphous materials. This is consistent with the amorphous wide peaks shown in the XRD patterns, confirming that the supports of SBA-15 and MCM-41 lack an ordered crystal structure, which is an essential feature of amorphous.

To study the structural characteristics of different all-silica supports, N₂ adsorption-desorption tests were conducted on four catalysts: PtZn/S-1, PtZn/S- β , PtZn/MCM-41, and PtZn/SBA-15. As shown in Figure 3, the adsorption-desorption isotherms of PtZn/S-1 and PtZn/S- β exhibit type I characteristics, which are typical isotherm behaviors of microporous materials^{27,28}. The isotherms of PtZn/SBA-15 and PtZn/MCM-41 exhibited the typical type IV characteristics of mesoporous materials. Pore structure parameters of different all-silica supported catalysts are shown in Table 1. The average pore size of PtZn/S-1 reached 9.6nm, significantly larger than the intrinsic micropore size of the S-1 molecular sieve, indicating that the S-1 molecular sieve is not a single micropore structure but a composite pore structure composed of a microporous framework and mesopores, and the accumulation of mesopores is the dominant factor contributing to its characteristic large pore size. PtZn/MCM-41 has the highest specific surface area, reaching 853m²/g, which is consistent with the high specific surface area intrinsic characteristics of MCM-41 mesoporous molecular sieves.

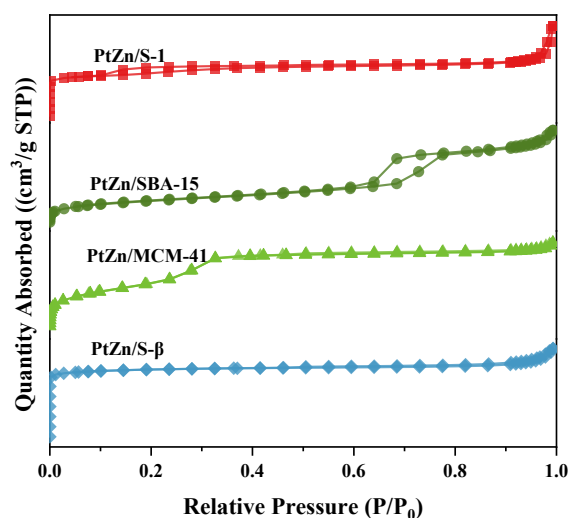


Fig.3. N₂ adsorption-desorption isotherms of different all-silica support catalysts.

Table 1. Change of reactant concentrations during esterification reaction

Sample	$S_{\text{BET}}^a(\text{m}^2/\text{g})$	$V_p^b(\text{cm}^3/\text{g})$	$D_p^c(\text{nm})$
PtZn/S-1	397	0.21	9.6
PtZn/SBA-15	626	0.93	7.3
PtZn/MCM-41	853	0.63	2.9
PtZn/S - beta	462	0.20	8.8

SBETa: BET surface area, V_{pb} : pore volume, D_{pc} : average diameter size

The H_2 -TPR was used to investigate the difficulty of reducing species in different all-silica supported catalysts. Generally, the reduction temperature of PtOx was lower ($<200^\circ\text{C}$), while that of ZnO was higher. As shown in Figure 4, all samples presented characteristic reduction peaks at around 450°C , which were located between the reduction temperatures of PtOx and ZnO, indicating that there was an electron or structure-level interaction between Pt and Zn species on the support surface, forming species with synergistic effects^{29,30}. The reduction temperature of PtZn/S-1 was significantly lower than that of the other samples, and the energy barrier required to overcome during the reduction process was lower, making it easier to be reduced to the catalytically active low-valent species, thus providing sufficient active sites for the reaction.

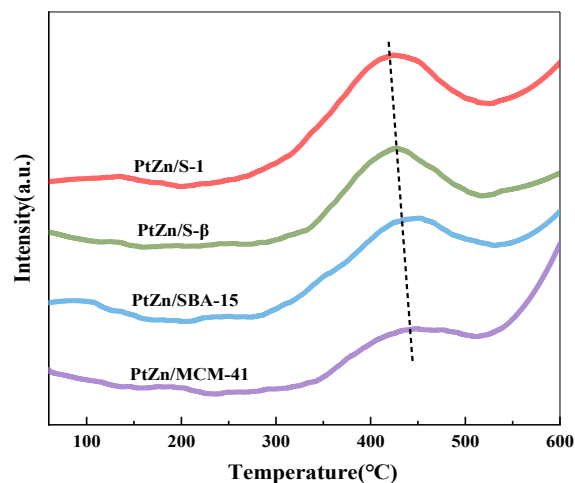


Fig.4. H_2 -TPR of different all-silica support catalysts.

To identify the types and distribution characteristics of hydroxyl groups on the surfaces of different all-silica supports, in-situ infrared was used to characterize the hydroxyl vibration of all-silica supports. According to existing literature reports³¹, the absorption peak at 3720cm^{-1} corresponds to the stretching vibration signal of the isolated hydroxyl group, while the absorption peak at 3500cm^{-1} belongs to the characteristic vibration signal of the hydroxyl nest. As shown in Figure 5, all supports showed the characteristic peak of the stretching vibration of the isolated hydroxyl group at 3720cm^{-1} , while in the characteristic vibration signal of the hydroxyl nest at 3500cm^{-1} , only the S-1 support showed a distinct absorption peak of the hydroxyl nest, and the SBA-15, MCM-41 and S- β support samples all showed significant characteristic peak signals. This result indicates that the enriched hydroxyl nest content of the S-1 support is significantly higher than that of the other all-silicon supports, while the hydroxyl nest species content of SBA-15, MCM-41 and S- β is very low or not effectively enriched. The hydroxyl nests on the surface of the support are usually key anchoring sites for the metal active component, and the difference in their content will directly affect the dispersion state and anchoring degree of Pt and Zn species.

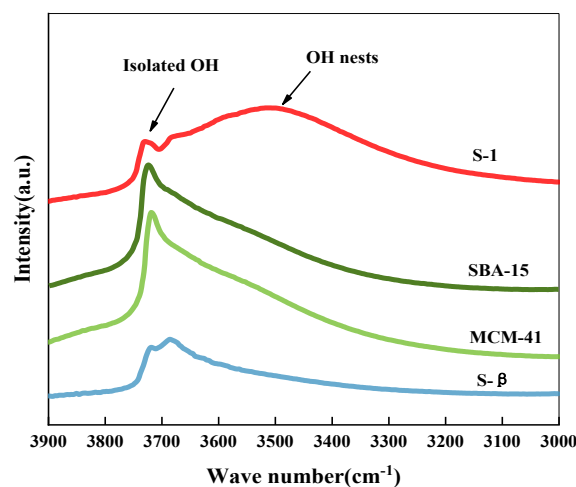


Fig.5. in-situ infrared spectra of different all-silica support catalyst.

To further clarify the mechanism of action of hydroxyl nests in the catalyst preparation process, Figure 6 compares the infrared spectral characteristics of pure S-1 supports with PtZn loaded PtZn/S-1 samples. The infrared spectroscopy results showed that the intensity of the characteristic peak belonging to the isolated hydroxyl group at 3720cm^{-1} did not change significantly, indicating that the PtZn component did not interact with the isolated hydroxyl

group on the support surface during loading, while the intensity of the strong absorption band corresponding to the hydroxyl group at 3500cm^{-1} was significantly weakened. In combination with similar phenomena reported in the literature^{32,33}, after the introduction of the metal component, most of the hydroxyl nest sites on the surface of the S-1 support were occupied by the active species, which led to a significant attenuation of the intensity of its characteristic vibration signal. From this, it can be inferred that the large number of hydroxyl nests enriched on the surface of the S-1 support provide sufficient anchoring sites for the PtZn active species. This structural advantage not only effectively promotes the uniform dispersion of the PtZn active components, but also significantly increases the exposure of the active sites.

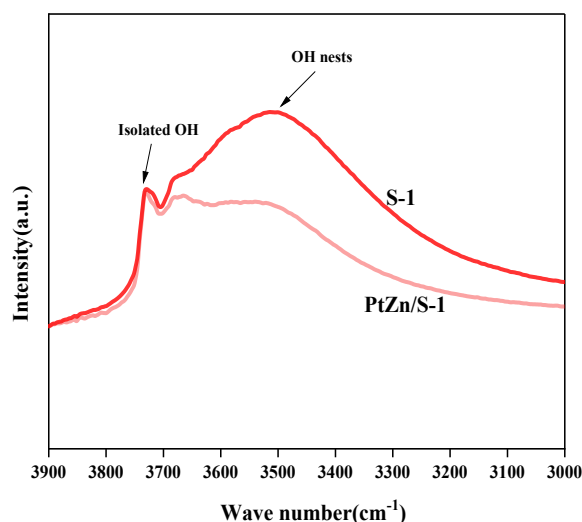


Fig.6. In situ infrared spectra of S-1 and PtZn/S-1 catalysts.

To determine the combination states of Pt species in different all-silica supported catalysts, XPS was used to characterize them, and the corresponding Pt 4f orbitals are shown in Figure 7. The spectra of the Pt 4f orbitals can be decomposed into two double peaks, indicating that the Pt species in the reduced catalyst do not exist in a single valence state but simultaneously contain both metallic (Pt^0) and oxidized (Pt^{2+}) forms. In combination with the data reported in the literature³⁴⁻³⁶, the binding energies corresponding to the $4f_{7/2}$ and $4f_{5/2}$ characteristic peaks are approximately 71.8 eV and 75.1 eV for Pt^0 , and 73.2 eV and 76.1 eV for Pt^{2+} , respectively. Studies have confirmed that metallic state Pt^0 species are typically regarded as active centers of PDH reactions, and the higher the proportion of Pt^0 , the better the PDH reaction activity of the catalyst^{37, 38}. The Pt^0 and Pt^{2+} characteristic peak area ratios

among the four catalysts were analyzed as shown in Table 2. The Pt^0 ratios for PtZn/S-1, PtZn/SBA-15, PtZn/MCM-41, and PtZn/S- β were 95.9%, 92.0%, 92.6%, and 94.2%, respectively. This result intuitively indicates that the highest content of metallic state Pt^0 species was formed in the PtZn/S-1 catalyst, and this valence distribution characteristic is the key structural reason for the optimal catalytic activity of PtZn/S-1.

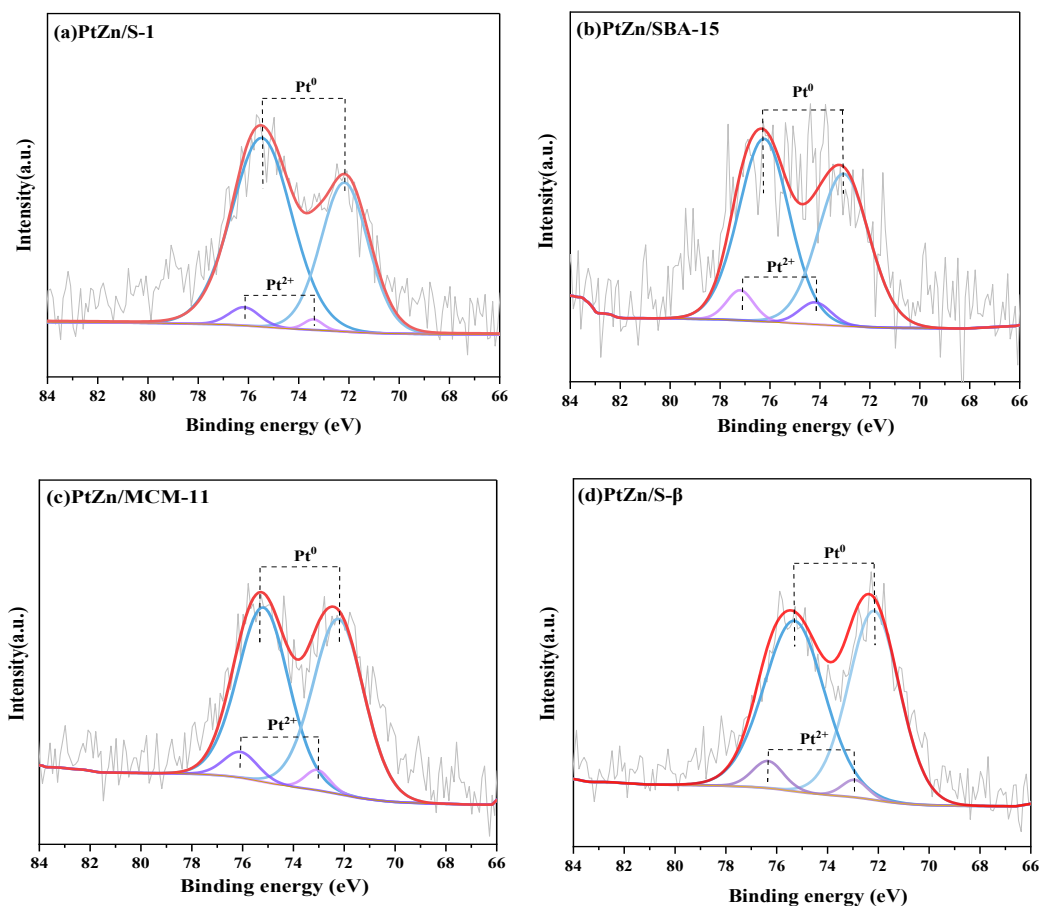


Fig.7. XPS spectra of Pt 4f orbitals on different all-silica support catalysts after reduction.

Table.2. Distribution of Pt species in different all-silica support catalysts after reduction

Sample	$\text{Pt}^0/(\text{Pt}^{2+}+\text{Pt}^0)$ (%)	$\text{Pt}^{2+}/(\text{Pt}^{2+}+\text{Pt}^0)$ (%)
PtZn/S-1	95.9	4.1
PtZn/SBA-15	92.0	8.0
PtZn/MCM-41	92.6	7.4
PtZn/S - beta	94.2	5.8

To investigate the carbon deposition of the PtZn/S-1 catalyst after PDH reaction, TG was used to characterize the catalyst samples. Figure 8 shows the TG curve of PtZn/S-1 after continuous reaction for 400 min. The results show that the thermal weight loss process of the PtZn/S-1 catalyst can be divided into two characteristic stages: the first stage of weight loss occurs in the range of 30 to 200 °C, which is attributed to the removal of adsorbed water on the catalyst surface. The second stage of weight loss occurs between 200 and 600 °C, with a carbon deposit of 0.76% in this range. The combined analysis shows that the PtZn/S-1 catalyst exhibits good thermal stability in the medium-high temperature range below 600 °C, where the mass change rate of the catalyst is slow and the total weight loss amplitude is small.

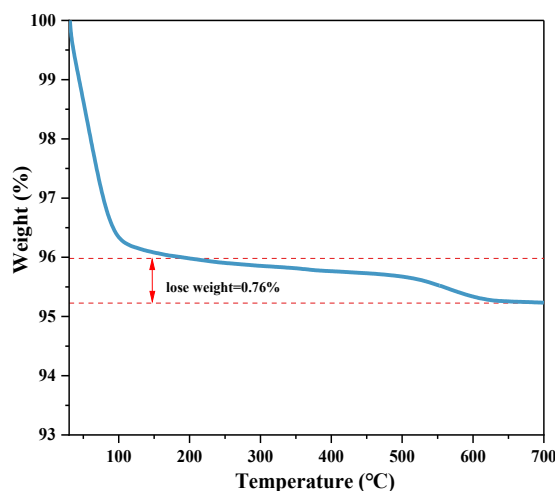


Fig.8. TG curves of the PtZn/S-1 catalyst.

Reaction Performance Evaluation

Figure 9 shows the PDH reaction performance of PtZn catalysts loaded on different all-silica supports. As shown in the figure, the PtZn/S-1 catalyst exhibits the best dehydrogenation activity, with a propane conversion of 29.1% and a propylene selectivity of 96.8%. In contrast, the propane conversion of PtZn/S- β , PtZn/SBA-15 and PtZn/MCM-41 catalysts decreased in sequence, with PtZn/MCM-41 having the lowest catalytic activity. Further analysis in combination with the characterization results revealed that metallic state Pt⁰ is the core active center of the PDH reaction, and the relative proportion of Pt⁰ in PtZn/S-1 was significantly higher than that in the other samples. The essence of this difference lies in the fact that the hydroxyl nest structure of the S-1 support provides sufficient active sites to

mediate the efficient dispersion and exposure of Pt^0 , thereby significantly enhancing the PDH reaction activity. The lower content of hydroxyl nests in PtZn/S- β , PtZn/SBA-15 and PtZn/MCM-41 catalysts leads to a reduction in the number of active sites and a decrease in Pt^0 exposure, ultimately resulting in a significant reduction in propane conversion.

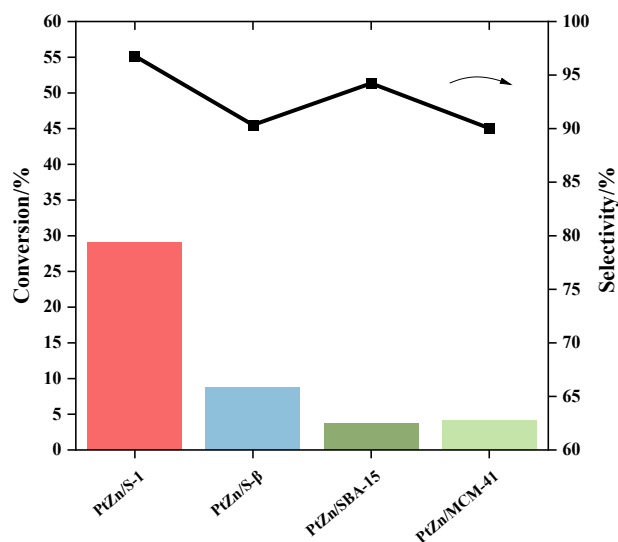


Fig.9. PDH activity test of different all-silica support catalysts, atmospheric pressure, 600°C $\text{C}_3\text{H}_8:\text{Ar}=4:6$, $\text{WHSV}=13.39\text{h}^{-1}$.

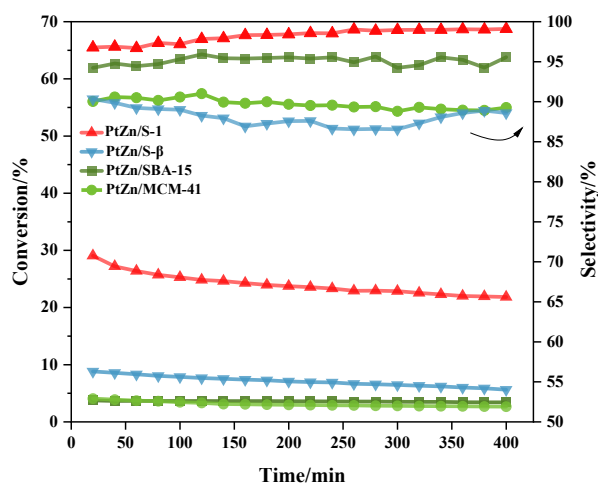


Fig.10. Stability tests of different all-silica support catalysts, atmospheric pressure, 600°C, $\text{C}_3\text{H}_8:\text{Ar}=4:6$, $\text{WHSV}=13.39\text{h}^{-1}$.

Stability test of PDH reaction of PtZn loaded on different all-silicon support was investigated in Figure 10. It can be seen from the figure that the initial conversion of PtZn/S-1 reached 29.1%, showing a slow decay trend as the reaction proceeded, and the conversion remained stable at 21.8% after 400 min, demonstrating the optimal activity stability. The initial conversion of PtZn/S- β was 8.8%, and it dropped to 5.6% after 400 minutes of reaction. The initial activity of PtZn/MCM-41 and PtZn/SBA-15 was lower, at 4.1% and 3.7% respectively, and they were rapidly deactivated as the reaction progressed, with conversions approaching 0% after 400 minutes, largely losing their catalytic activity. Table 3 shows the deactivation parameters of each catalyst after 400 min of reaction. The deactivation parameter of PtZn/S-1 was only 25.1%, significantly lower than that of PtZn/S- β . According to the results of the catalytic activity evaluation, PtZn/S-1 has both high initial activity, high propylene selectivity and long-term stability of slow deactivation, and is the best-performing sample among the PtZn series catalysts supported on all-silica supports.

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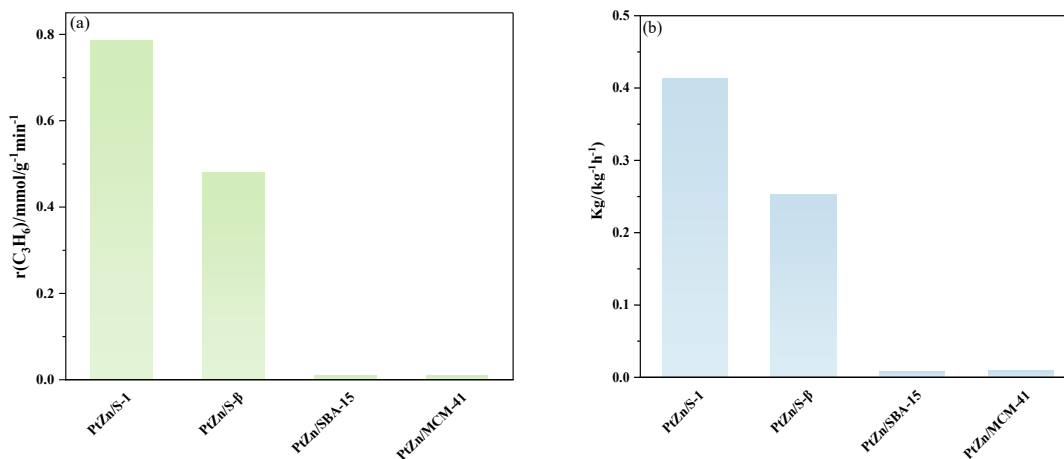
Table.3. Initial conversions (Xa), final conversions (Xb), deactivation parameters (Da), Initial selectivity (Sa)

365

Sample	X _a (%)	X _b (%)	D ^a	S _a (%)
PtZn/S-1	29.1	21.8	25.1	96.8
PtZn/S - beta	8.8	5.6	36.4	90.3
PtZn/MCM-41	4.1	0	/	90.1
PtZn/SBA-15	3.7	0	/	94.2

Da=(Xa-Xb)/Xa × 100%

367



368

369 **Fig.11.** Different fully siliceous support catalysts (a) conversion, (b) space-time yield,
 370 atmospheric pressure, 600°C, C₃H₈:Ar=4:6, WHSV=13.39h⁻¹.

371

372

373 Figure 11(a) shows the propylene generation rate of PtZn loaded on different all-silica
 374 supports. It can be seen from the figure that the propylene generation rate of PtZn/S-1 is
 375 significantly optimal, reaching 0.79 mmol·g⁻¹·min⁻¹. Next is the PtZn/S-β catalyst, with a
 376 propylene generation rate of 0.48 mmol·g⁻¹·min⁻¹. The data of PtZn/SBA-15 and PtZn/MCM-
 377 41 were extremely low, almost zero, indicating that they basically had no ability to effectively
 378 catalyze the PDH reaction. The results further confirm the excellent PDH reaction catalytic
 379 performance of PtZn/S-1, with the full exposure of Pt⁰ mediated by the hydroxyl nest-
 380 mediated support, which ensures the efficient activation and conversion of propane while
 381 effectively suppressing the occurrence of side reactions, thus achieving a high rate of
 382 propylene generation.

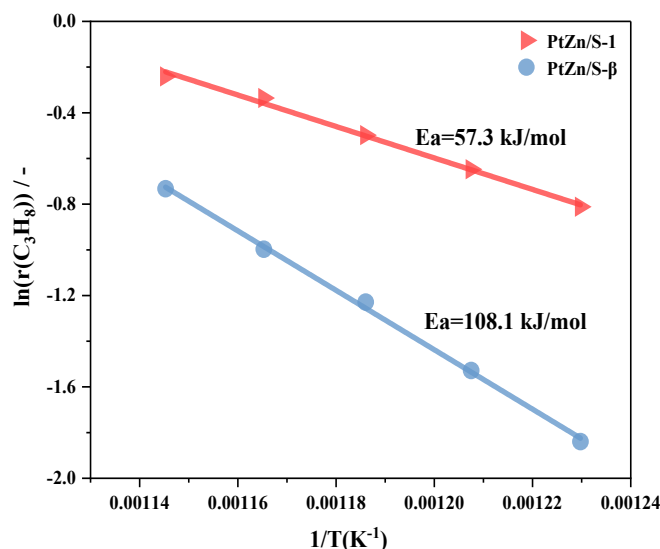
383

Figure 11(b) shows the spatiotemporal yields of PtZn loaded on different all-silica
 384 supports. The results show that PtZn/S-1 has the highest spatiotemporal yield at 0.41 kg·kg⁻¹
 385 h⁻¹, followed by PtZn/S-β at 0.25 kg·kg⁻¹·h⁻¹. The spatiotemporal yields of PtZn/SBA-15 and
 386 PtZn/MCM-41 were close to zero, significantly lower than the former two. Combined with
 387 the previous characterization results, it can be known that the enrichment of hydroxyl nest
 388 characteristics of the S-1 support can promote the full exposure of the active site, accelerate
 389 the rapid desorption and diffusion of propylene, effectively inhibit the coverage of the active
 390 site by side reactions such as carbon deposition, and ultimately make PtZn/S-1 show better
 391 spatiotemporal yields.

392

Figure 12 shows a linear relationship between ln(r) (the natural logarithm of the
 393 reaction rate) of PtZn/S-1 and PtZn/S-β catalysts and 1/T(the reciprocal of temperature) . The
 394 reaction temperature gradients are 540, 555, 570, 585 and 600°C. It can be seen from the
 395 figure that ln(r) and 1/T of PtZn/S-1 and PtZn/S-β catalysts both show good linear fitting. The
 396 activation energy of PtZn/S-1 is 57.3 kJ/mol. Compared with PtZn/S-β, the activation energy
 397 of PtZn/S-1 is significantly lower, indicating that the corresponding PDH reaction energy
 398 barrier is lower, making the activation and dehydrogenation of propane molecules more likely
 399 to occur, thereby significantly increasing the catalytic reaction rate. This result further
 400 confirms that the structure and distribution of the active sites in the PtZn/S-1 catalyst are more

suitable for the energy barrier requirements of the PDH reaction, which is one of the key reasons for its superior catalytic performance.



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Fig.12. Arrhenius curves of PtZn/S-1 and PtZn/S-β at atmospheric pressure, 600°C, C₃H₈:Ar=4:6, WHSV=13.39h⁻¹.

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Conclusions

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In this paper, four all-silica materials with typical structural differences (S-1, S-β, MCM-41, SBA-15) were used as supports to prepare a series of PtZn-supported catalysts by co-impregnation, combined with XRD, N₂ adsorption-desorption, in-situ infrared diffuse reflection, XPS, TG characterization and fixed-bed PDH performance testing. The regulation mechanism of the structure of all-silica supports on the active centers and catalytic performance of the catalysts was systematically investigated. Characterization results indicated that the S-1 support had the highest hydroxyl nest content, providing sufficient anchor sites for the PtZn active component, promoting uniform dispersion of the active component and increasing Pt⁰ exposure (95.9%), while the S-β, MCM-41 and SBA-15 supports had very low hydroxyl nest content, with Pt⁰ accounting for less than 95%. Catalytic performance tests showed that the PtZn/S-1 catalyst exhibited the best PDH performance at 600°C and WHSV=13.39h⁻¹: propane conversion rate 29.1%, propylene selectivity 96.8%, initial propylene generation rate 0.79 mmol·g⁻¹·min⁻¹, significantly superior to the other three

catalysts. According to the analysis, the hydroxyl nest structure of the all-silica support is a key factor in regulating the dispersion of the active center and the electronic state of PtZn, and its content directly determines the exposure and catalytic performance of Pt⁰. This study identifies the core role of the hydroxyl nest structure in all-silica support-supported PtZn catalysts, providing new insights for the directional design of efficient PDH catalysts.

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