

Ultrafine Pt-Sn intermetallic catalyst constructed in β zeolite for long-chain alkane dehydrogenation.

Ying Qiu¹, Jianchao Liu¹, Mingge Zhang¹, Yu Liang²(✉), Lei Liu¹(✉), Jinxiang Dong¹

¹ Shanxi Key Laboratory of Chemical Product Engineering, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

² Shanxi Key Laboratory of Bioagent Utilization and Eco-Pesticide Innovation, College of Plant Protection, Shanxi Agricultural University, Taigu 030801, China

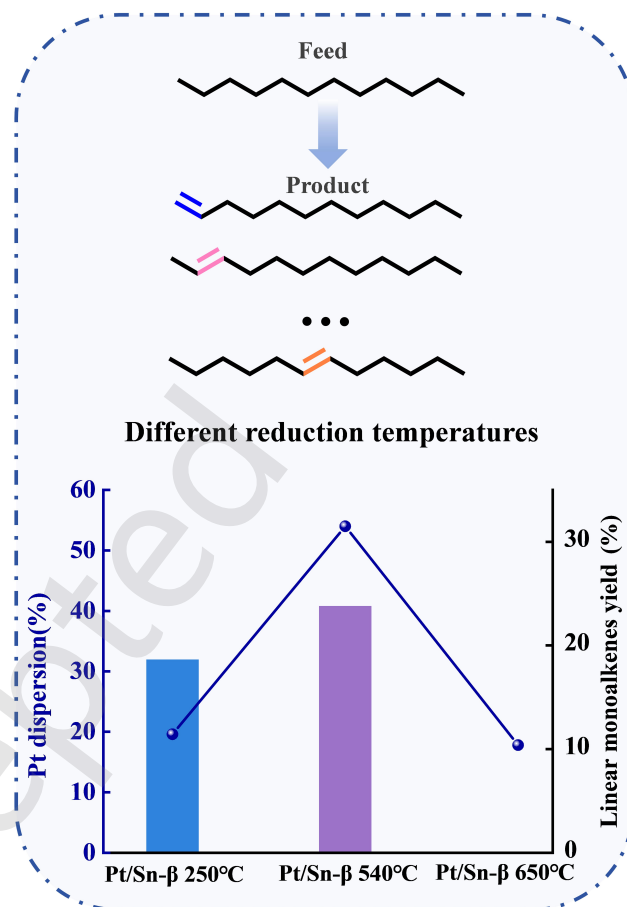
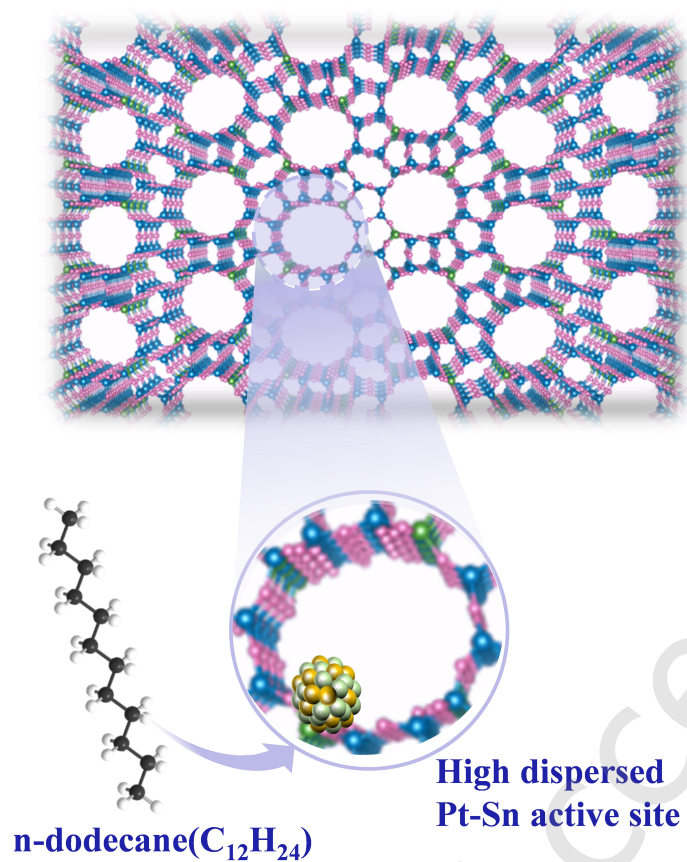
Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909180>

<https://www.sciopen.com/journal/1998-0124> on Sep. 8, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Catalyst structure of Pt/Sn- β 

Zeolite confinement coupled with reduction-temperature-controlled Sn precipitation yields highly dispersed Pt-Sn intermetallic sites on β zeolite for efficient n-dodecane dehydrogenation with high product formation rates.

Ultrafine Pt-Sn intermetallic catalyst constructed in β zeolite for long-chain alkane dehydrogenation.

Ying Qiu¹, Jianchao Liu¹, Mingge Zhang¹, Yu Liang²✉, Lei Liu¹✉, and Jinxiang Dong¹

¹ Shanxi Key Laboratory of Chemical Product Engineering, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

² Shanxi Key Laboratory of Bioagent Utilization and Eco-Pesticide Innovation, College of Plant Protection, Shanxi Agricultural University, Taigu 030801, China

Received: 1 June 2026; Revised: 5 September 2026; Accepted: 8 September 2026

✉ Address correspondence to Lei Liu, liulei@tyut.edu.cn; Yu Liang, liangyu94@sxau.edu.cn.

 Cite this article: Nano Research, 2026, 19, 94909180 <https://doi.org/10.26599/NR.2026.94909180>

ABSTRACT: The dehydrogenation of n-dodecane is industrially significant, yet Pt-Sn catalysts widely used for this reaction are often limited by poorly controlled Pt-Sn interactions and ill-defined metal chemical states. Here, a Pt-Sn/ β zeolite catalyst is constructed by grafting Sn onto dealuminated β zeolite via Si–O–Sn bonds, followed by reduction-controlled Sn precipitation that drives dynamic Pt re-dispersion. XRD, HRTEM, XPS, XAFS and *in situ* DRIFTS confirm that this process generates well-dispersed Pt-Sn intermetallic active sites at 540 °C, with enhanced bimetallic modulation and geometric isolation. The optimized catalyst achieves a product formation rate of 0.00714 mol g^{−1} s^{−1}. These findings establish reduction-temperature-controlled Sn precipitation as an effective strategy for tuning Pt-Sn active sites and offer a practical design principle for efficient long-chain alkane dehydrogenation catalysts.

KEYWORDS: n-dodecane dehydrogenation; Pt-Sn catalyst; β zeolite; intermetallic sites; reduction temperature.

1. Introduction

Against the backdrop of the ongoing transformation in the energy and chemical industries, the deep processing of petroleum fractions and coal liquefaction products represents a critical pathway toward efficient resource utilization and industrial chain extension [1, 2]. Light alkane dehydrogenation has advanced considerably, and propane dehydrogenation (PDH) to propylene is now well established as a mainstream petrochemical route with mature catalyst and process technologies [3]. In contrast, direct dehydrogenation of long-chain alkanes (C10+) to olefins has received limited attention, despite olefin intermediates being key building blocks in alkylation chemistry for chain extension and functional upgrading. These olefins are valuable precursors for synthetic detergents, plasticizers, lubricant additives, and polymer monomers [4-6]. Currently, long-chain olefins are produced industrially via ethylene oligomerization or wax cracking, both of which suffer from poor atom economy, broad product distributions, and high separation costs [7]. Direct dehydrogenation offers high atom utilization and process simplicity, yet rational catalyst design has received little systematic study.

The superior C–H activation capability of Pt-based catalysts has led to their widespread use in PDH; however, these catalysts still suffer from sintering, poor selectivity, and rapid coking-induced deactivation at high temperatures [8].

Introducing a second metal component (such as Sn [9], Ir [10], Zn [11], In [12], Fe [5], Ga [13], or Cu [14]) to form bimetallic systems has emerged as an effective means of improving Pt catalyst performance. For example, Xu et al. tuned the b-axis length of the Silicalite-1 support to control Pt-Sn₂ monomer migration within zeolite channels [15]. Shi et al. stabilized Pt-Sn clusters on γ -Al₂O₃ nanosheets rich in pentacoordinate aluminum sites, achieving high electron density on Pt sites and excellent propane dehydrogenation performance [8]. The superior performance of Pt-Sn systems in alkane dehydrogenation is mainly attributed to Sn-induced d-electron donation and the site-isolation effect [16-18]. These effects downshift the Pt d-band center, weaken alkene adsorption, and suppress C–C cleavage and coke formation on contiguous Pt ensembles, thereby enhancing selectivity and long-term stability.

The application of Pt-Sn systems to long-chain alkane dehydrogenation remains challenging. When n-dodecane is employed as a model substrate, the reaction demands careful control of both support properties and active-site structure. Acidic sites catalyze side reactions such as isomerization and aromatization, whereas larger Pt particles promote deep dehydrogenation of mono-olefins to dienes or aromatics [5, 19]. To overcome these obstacles, beta zeolite (β) offers a viable and promising alternative, with its three-dimensional 12-membered ring channels facilitating diffusion of long-chain molecules such as dodecane [5, 20], while dealumination allows precise tuning of acidity to

suppress cracking and coking without compromising framework stability. Coupled with the confinement effect that stabilizes metal cations [21], these features enable β zeolite to reconcile macromolecular diffusion with side- reaction suppression, positioning it as one of the most functionally compatible supports for long- chain alkane dehydrogenation.

Herein, an ultrafine Pt-Sn intermetallic catalyst is constructed within dealuminated β zeolite to address the lack of systematic studies on long- chain alkane dehydrogenation. By finely tuning the reduction temperature, the chemical state and microstructure of Pt-Sn species are tailored to form well-defined ultrafine intermetallic species, enabling simultaneous optimization of active- site dispersion and surface acid-base properties. Using n- dodecane as a model substrate, structure-performance correlations are systematically established, and the respective roles of the intermetallic structure and zeolite confinement in governing olefin selectivity and catalyst stability are elucidated.

2. Experimental

2.1. Catalyst preparation

Commercial Al- β zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was used as the starting material. The framework aluminum was removed by nitric acid treatment to obtain the dealuminated zeolite support, which was denoted as Si- β . Tin species were introduced via a solid-state thermal diffusion method. The Si- β powder was first mechanically mixed with $\text{Sn}(\text{CH}_3\text{COO})_2$ at a Si/Sn molar ratio of 15:1. The mixture was calcined at 823 K for 3 h under argon and then calcined in air for another 3 h to yield Sn- β . $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.5 wt% Pt) and KCl (0.5 wt% K) were deposited on Sn- β by incipient wetness. Impregnated samples were dried (353 K, 12 h) and calcined (823 K, 2 h), yielding Pt/Sn- β . Detailed conditions are provided in S1.

2.2. Catalyst characterization

The crystalline phases of the as-prepared samples were examined by XRD (Rigaku Ultima IV). Textural properties were determined by N_2 sorption at liquid nitrogen temperature using a Micromeritics ASAP 2020 analyzer. The elemental contents were measured by ICP-OES (Avio 500, PerkinElmer). Diffuse reflectance UV-vis spectra were recorded on a Lambda 650 spectrometer. HRTEM images were acquired using a JEM-F200 microscope operated at an accelerating voltage of 200 kV. Surface elemental states and chemical environments were further analyzed by XPS (Thermo Scientific ESCALAB 250Xi). Additionally, NH_3 -TPD, H_2 -TPR, and H_2 pulse chemisorption measurements were performed on an AutoChem II 2920 (Micromeritics) equipped with a thermal conductivity detector (TCD) to evaluate acidity, basicity, reducibility, and metal dispersion, respectively. Pt L_3 -edge XAFS measurements were performed at the BL14W beamline of the Shanghai Synchrotron Radiation Facility (SSRF).

Pyridine adsorption infrared spectroscopy (Py-IR) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were both conducted on a Bruker INVENIO R spectrometer. The former was used to identify and quantify Brønsted and Lewis acid sites, whereas the

latter examined the catalyst surface under an H_2 atmosphere to mimic n-dodecane dehydrogenation conditions. Detailed measurement conditions are provided in S2.

2.3. N-dodecane dehydrogenation

The catalyst (40–60 mesh) was mixed with quartz sand, charged into a quartz fixed-bed reactor (8 mm), and reduced in situ under H_2 flow for 2 h. N-dodecane dehydrogenation was subsequently conducted under atmospheric pressure. After the reactor was heated to 470 °C, liquid dodecane was pumped at 0.2 mL/min, vaporized by preheating, and fed into the quartz tube. The molar feed rate per unit mass of Pt, denoted as S , was $0.00733 \text{ mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$. Liquid products were collected and subsequently analyzed by GC (Agilent 7820A) with an FID detector and an HP- PONA column. Product identification was performed using a GCMS-QP2010 Ultra. The conversion of n-dodecane (X_d), the selectivity for linear mono-dodecenes (S_i), and the formation rate of mono-dodecene products (r_i) were calculated based on the external standard method and chromatographic peak areas, according to the following equations (1), (2), and (3):

$$\begin{aligned} (1) \quad X_d(\%) &= (1 - C_{A, \text{final}} / C_{A, \text{initial}}) \times 100\% \\ (2) \quad S_i(\%) &= (A_p / \sum A_{\text{all products}}) \times 100\% \\ (3) \quad r_i &= X_d \times S_i \times S \end{aligned}$$

In these equations, $C_{A, \text{initial}}$ and $C_{A, \text{final}}$ represent the concentrations of n-dodecane in the feed before reaction and in the collected liquid product after reaction, respectively. Both concentrations were quantified by GC-FID using an external-standard calibration curve. A_p represents the GC peak area of the linear mono-dodecene product, while $A_{\text{all-products}}$ represents the sum of the GC peak areas of all detected products.

3. Results and discussion

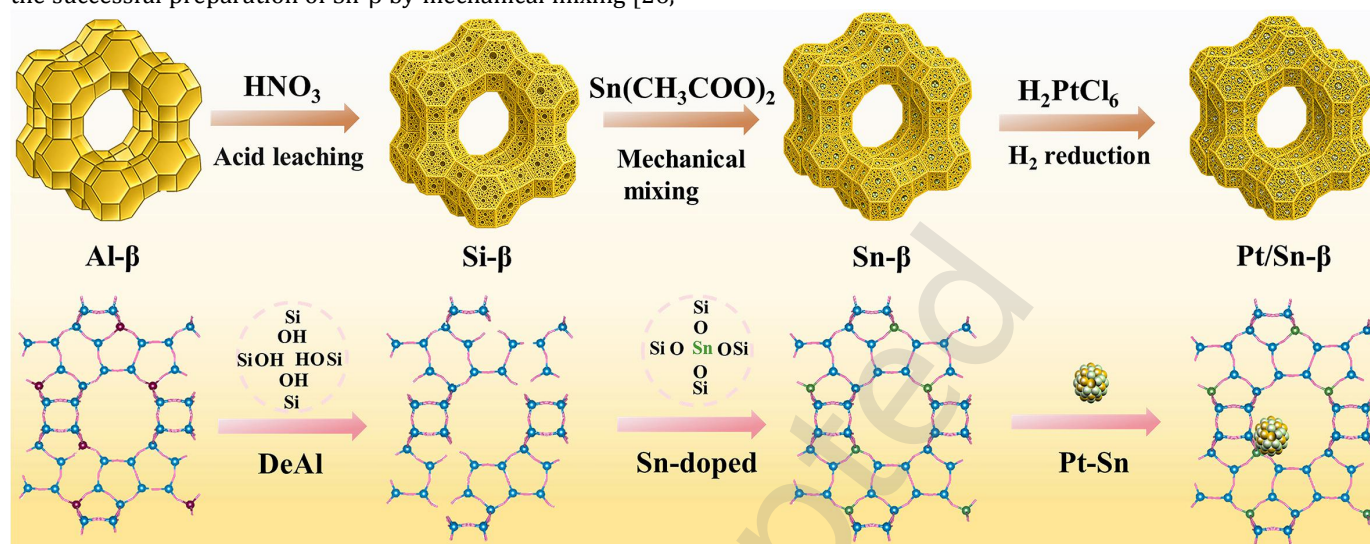
3.1. Structural characteristics

The catalyst preparation procedure is illustrated in Scheme 1. First, β zeolite was dealuminated with nitric acid to remove framework Al and generate silanol nests (Si-OH). Subsequently, the zeolite was mechanically mixed with $\text{Sn}(\text{CH}_3\text{COO})_2$ and subjected to sequential calcination: first at 823 K under an inert atmosphere to decompose the acetate, and then at the same temperature in air to remove residual carbon, ultimately forming Si-O-Sn bonds at the former framework Al sites. After Pt loading and subsequent reduction, Pt-Sn bimetallic active sites were expected to be dispersed on the zeolite framework.

The structural evolution of the zeolite support and derived catalysts was investigated by XRD. The patterns of H- β , Si- β , and Sn- β are shown in Fig. S1, while those of the catalysts reduced at different temperatures are presented in Fig. 1a. All samples retained the characteristic reflections of the BEA topology [22], indicating that the zeolite framework remained intact during dealumination and metal incorporation. ICP results in Table S1 showed that Al was almost completely removed. As shown in Fig. S1, after dealumination, the main reflection shifted from $2\theta = 22.54^\circ$ for H- β to 22.82° for Si- β [20, 22, 23], indicating lattice contraction. After Sn introduction, the peak shifted back to

22.54°, suggesting lattice expansion. This shift may result from the condensation of Sn species with the silanol nests formed during dealumination to produce Si–O–Sn linkages. The longer Sn–O bonds relative to Si–O bonds increase the local interatomic distances, leading to partial framework reconstruction and lattice expansion [24, 25]. The $n(\text{Si})/n(\text{Sn})$ ratio of approximately 15:1 further supported the successful preparation of Sn- β by mechanical mixing [26,

27]. No metallic Pt reflections were detected, likely because of the high Pt dispersion. As shown in Fig. 1a, no metallic Sn reflections were observed after reduction at 250 °C, whereas they appeared and gradually intensified at 540 and 650 °C. These results suggest that higher reduction temperatures promote the reduction and exsolution of framework Sn species, resulting in the formation of metallic Sn particles.



Scheme 1. Synthesis scheme of Pt and Sn-based catalysts

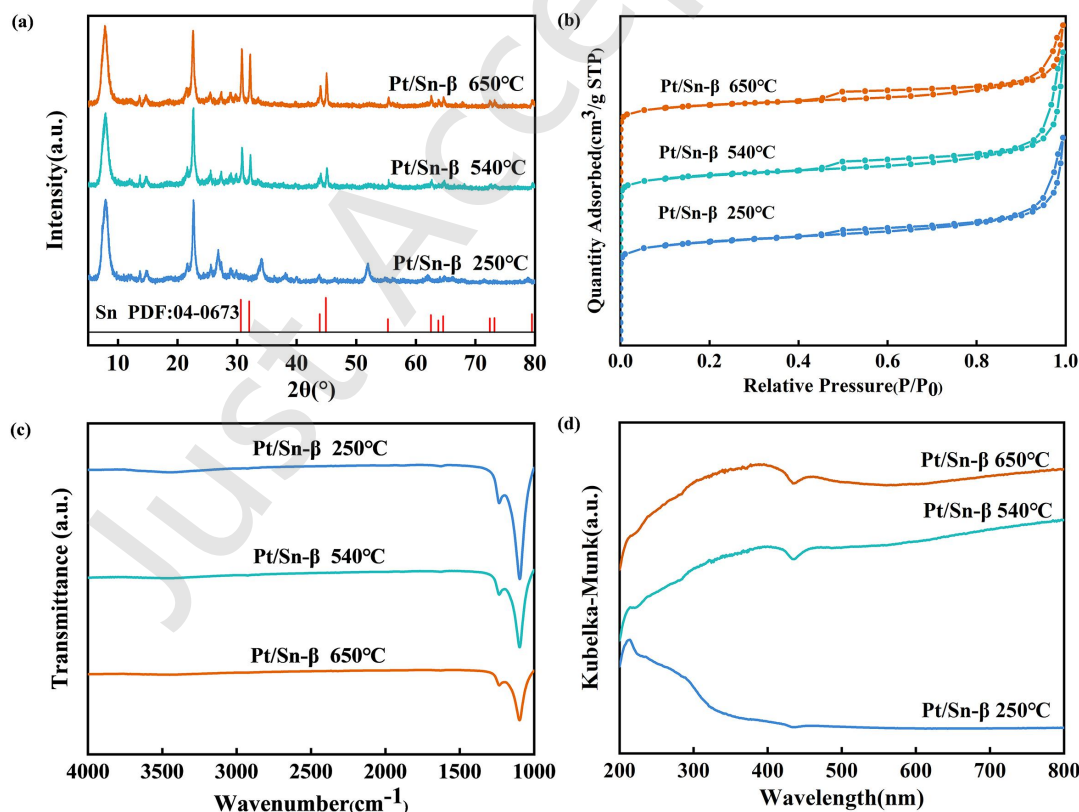


Fig. 1. X-ray diffraction patterns (a), N_2 adsorption-desorption isotherms (b), FT-IR spectra (c), and UV-vis spectra (d) of the catalysts reduced at different temperatures.

Fig. 1b and Fig. S2 present the N_2 adsorption-desorption isotherms of the catalysts and corresponding supports (H- β , Si- β , and Sn- β), respectively. All samples exhibited predominantly Type I isotherms, confirming the microporous structure of β zeolite. The N_2 uptake at $P/P_0 < 0.1$ was attributed to micropore filling [20, 23], whereas that at $P/P_0 > 0.9$ mainly arose from interparticle voids [24]. A

weak hysteresis in the intermediate relative-pressure region became more pronounced after dealumination from H- β to Si- β , suggesting the generation of secondary porosity (Fig. S2). The textural properties are summarized in Table S1. Compared with H- β , Si- β showed a lower specific surface area, while its total pore volume increased from 0.39 to 0.42 cm^3/g . Specifically, the micropore volume contracted (0.20

→ 0.17 cm³/g) and mesopore volume expanded (0.19 → 0.25 cm³/g). Together, these changes reflect the generation of defects and secondary porosity during dealumination [25], and the largely retained after Sn incorporation. Thus, the hierarchical pore structure of Sn-β may improve the accessibility of Pt-Sn species and facilitate the diffusion of bulky n-dodecane and olefin products. The Pt/Sn-β sample reduced at 650 °C (Fig. 1b) exhibited the most pronounced structural degradation, as evidenced by the lowest specific surface area and total pore volume, suggesting that high-temperature reduction intensified pore blockage and framework damage.

Fig. 1c and Fig. S3 present the FT-IR spectra of the catalysts and corresponding supports (H-β, Si-β, and Sn-β), respectively. For H-β, the intense band centered at 1093 cm⁻¹, accompanied by a weak shoulder at 1230 cm⁻¹, is assigned to

the asymmetric stretching vibrations of framework T-O-T bonds in TO₄ (T = Si or Al) tetrahedra [28, 29]. After dealumination (Fig. S3), the intensity of the main framework band increased, which is attributed to the removal of framework Al species and the increased relative contribution of Si-O-Si linkages, indicating a more siliceous framework environment [30]. After Sn introduction (Fig. S3), the intensity of this framework band decreased, suggesting that Sn introduction perturbed the local framework environment of dealuminated β [31]. After Pt loading and reduction at different temperatures (Fig. 1c), no obvious new vibration bands were observed. Instead, the intensity of the main framework band gradually decreased with increasing reduction temperature, indicating progressive changes in the local framework environment under reductive treatment.

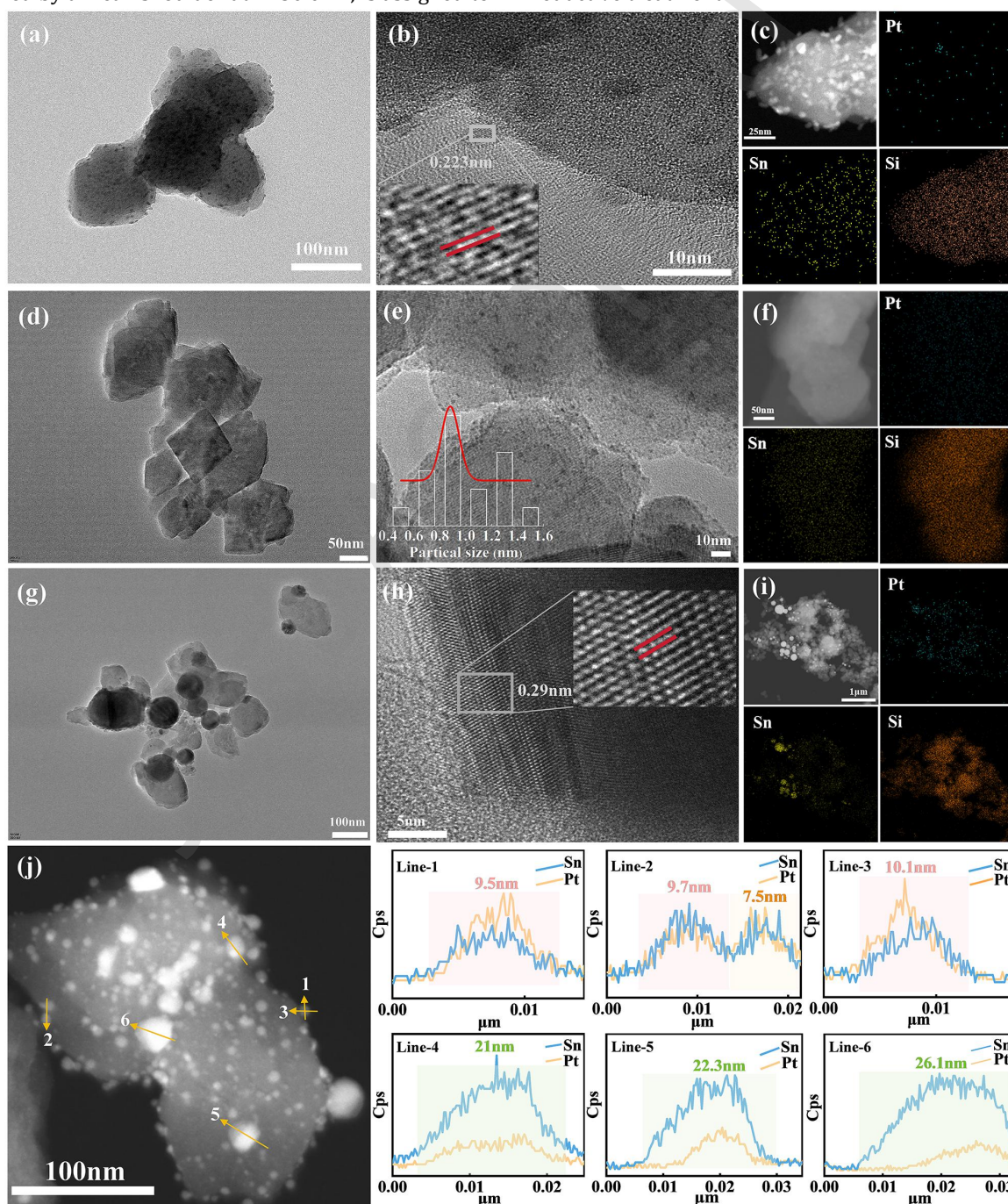


Fig. 2. HRTEM and corresponding elemental Mapping images of the catalysts reduced at different temperatures: 250 °C (a-c), 540 °C (d-f), and 650 °C (g-i), with the corresponding line-scan profile (j).

Fig. 1d and Fig. S4 show the UV-vis spectra of the Pt/Sn- β catalyst reduced at different temperatures and, the Sn- β support, and SnO₂- β as a reference, respectively. The absorption band below 250 nm is attributed to framework-isolated tetrahedral Sn species ($O^{2-} \rightarrow Sn^{4+}$ ligand-to-metal charge transfer), while the broad band above 250 nm also observed for SnO₂- β (Fig. S4), is assigned to extra-framework Sn species derived from framework Sn during reduction [32, 33]. The Sn- β (Fig. S4) support exhibited a strong absorption band at 207 nm, with no obvious absorption peak observed above 250 nm. When the Pt/Sn- β catalyst was reduced at 250 °C (Fig. 1d), an absorption band began to appear above 250 nm. As the reduction temperature increased to 540 °C and 650 °C, the broad absorption band above 250 nm significantly intensified, extending to 400 nm. These results indicate that the post-synthetic method successfully introduced Sn species into the β zeolite framework as highly dispersed isolated sites [33], and that increasing the reduction temperature of Pt/Sn- β promotes the exsolution of Sn species from the framework, with the degree of exsolution increasing with temperature.

HRTEM and elemental mapping (Fig. 2, Fig S5) analyses were performed for Pt/Sn- β to examine the β -zeolite morphology and Pt-Sn nanoparticle dispersion. Fig. 2 (a-c) and Fig. S5 (a) present the morphology and structural characterization of the catalyst reduced at 250 °C. The particle size distribution statistics indicated that the average particle size was 6.78 nm, while high-resolution imaging (Fig. 2b) revealed clear lattice fringes with an interplanar spacing of 0.223 nm, corresponding to the Pt (111) plane [34], thereby confirming the presence of metallic Pt nanoparticles. Elemental mapping (Fig. 2c) further indicated significant Pt agglomeration, with weak spatial correlation between Sn and Pt-enriched regions. H₂ pulse chemisorption measurements at different reduction temperatures in Fig. S6 showed that the Pt dispersion was only 19.59%, indicating a substantial reduction in the number of surface active sites available for catalysis. When the reduction temperature was further increased to 540 °C, Fig. 2 (d-f) revealed that the Pt-Sn intermetallic particles evolved into ultrafine ones with an average size of only 0.98 nm, exhibiting the smallest particle size and the most uniform distribution, although localized Sn enrichment was occasionally observed (Fig. S5b). Under these conditions, Pt dispersion reached a maximum value of 54% (Fig. S6), corresponding to the highest density of active sites [35]. By contrast, at a reduction temperature of 650 °C, pronounced particle growth and Sn-rich aggregation were observed (Fig. 2g-j and S5c). The lattice spacing of 0.29 nm observed in Fig. 2h was assigned to the Sn (200) plane, supporting the formation of Sn-rich particles. Line scans across particles of increasing size (Fig. 2j) showed largely overlapping Pt and Sn signals in smaller particles, whereas Sn appeared preferentially at the particle edges and Pt remained concentrated in the center as the particle size increased, indicating progressive elemental segregation and partial encapsulation of Pt by Sn-rich species [36, 37]. Consequently, the Pt dispersion sharply decreased to 17.8% (Fig. S6), and the active structure of the catalyst was

significantly degraded. Therefore, reduction at 540 °C promoted Pt-Sn interaction and Pt redispersion, yielding ultrafine, uniformly dispersed Pt-Sn species.

3.2. Surface properties of catalysts

Surface acidity was characterized by NH₃-TPD (Figs. 3a and S7) and pyridine-adsorbed infrared spectroscopy (Py-IR, Figs. 3b and S8) for the catalysts and corresponding supports (H- β , Si- β , and Sn- β). Based on the NH₃ desorption temperatures, the acid sites were classified as weak (100-250°C), medium-strength (250-350°C), and strong acid sites, with desorption signals above 350 °C assigned to strong acid sites [38, 39]. The corresponding acid site concentrations are summarized in Table S2. Py-IR analysis (Table S2) showed that the H- β support contained 0.201 mmol g⁻¹ of Brønsted acid sites [40], whereas no appreciable Brønsted acidity was detected after dealumination, confirming the removal of framework Al-associated acid sites. The remaining acidity was therefore mainly related to Lewis-acidic Sn species. After reduction at 250 °C, Pt/Sn- β contained abundant strongly adsorbing acid sites. HRTEM (Fig. 2a-c) showed aggregated Pt particles and weak spatial association between Pt and Sn, suggesting that a considerable fraction of Sn remained spatially separated from Pt as isolated or oxidized species. These Sn environments likely contributed to the formation of abundant strong acid sites, which may promote cracking and isomerization reactions [41]. Increasing the reduction temperature to 540 °C decreased the total acidity from 2425 to 1099.72 μ mol g⁻¹ (Table S2), with medium-strength acid sites becoming predominant. Meanwhile, quantitative Py-IR analysis showed that the Lewis acid concentration increased from 0.041 to 0.057 mmol g⁻¹, indicating that Lewis-acidic Sn sites were retained and their concentration moderately increased despite the substantial decrease in total acidity. HRTEM (Fig. 2d-f) revealed ultrafine, highly dispersed Pt-Sn species, suggesting that Sn migration and Pt-Sn interactions promoted the reorganization of surface Sn species and reduced heterogeneous strongly adsorbing sites [42,43]. At 650 °C, the total acidity further decreased to 713.22 μ mol g⁻¹, and the Lewis acid concentration sharply declined to 0.003 mmol g⁻¹ (Table S2). XRD (Fig. 1a) and HRTEM (Fig. 2g-j) indicated Sn aggregation and partial coverage of Pt, which reduced the number of Sn-related Lewis acid centers. Thus, reduction at 540 °C suppressed excessive strongly adsorbing acid sites while retaining an appropriate amount of Lewis acid centers, achieving a favorable balance between acidity and active structure.

Different degrees of Sn reduction lead to distinct interactions with Pt. Therefore, H₂-TPR characterization was employed to systematically evaluate the reducibility of Sn species. Fig. 3c presents the H₂-TPR profiles of the Sn- β support and Pt/Sn- β catalysts reduced at different temperatures, while the profile of unreduced Pt/Sn- β is shown in Fig. S9. Two distinct reduction peaks were observed for unreduced Pt/Sn- β . The first-stage reduction occurred in the range of 308-433 °C, while the second-stage reduction took place between 433 and 735 °C. Because Pt species are generally reduced below 300 °C, Pt in Pt/Sn- β

should be present in the metallic state; thus, the detected peaks can be ascribed exclusively to the reduction of Sn species [44]. The first reduction peak corresponded to the $\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$ reduction, and the second peak to the $\text{Sn}^{2+} \rightarrow \text{Sn}^0$ reduction [26, 45, 46]. Compared with the Sn- β (Fig. 3c) support without Pt, the reduction temperature of Pt/Sn- β decreased, indicating that Pt incorporation significantly promoted the reduction of Sn species and facilitated the formation of a Pt-Sn bimetallic phase [47]. After reduction at 250 °C (Fig. 3c), Sn species were not sufficiently reduced, leaving abundant $\text{Sn}^{4+}/\text{Sn}^{2+}$ species and hindering the development of optimal Pt-Sn interactions. In contrast, treatment at 540 °C (Fig. 3c) promoted further reduction of Sn species, which facilitated the formation of Pt-Sn interfacial interactions and generated a more favorable active structure for dehydrogenation.

As a structural promoter, Sn modifies the electronic environment of Pt through Pt-Sn interactions and contributes to the stabilization of Pt species. Accordingly, Sn 3d XPS spectra under different reduction temperatures are shown in Fig. 3(d-f), with spin-orbit coupling doublets corresponding to Sn 3d_{5/2} (484.8 eV) and Sn 3d_{3/2} (493.2 eV) [26]. The Pt 4f XPS spectra of the catalysts are provided in Figs. S10-S12. Due to the low Pt loading and high dispersion

of Pt species, the Pt 4f signals were relatively weak, preventing reliable quantitative analysis of the Pt chemical states. The Sn valence state in Pt/Sn- β changed markedly with increasing reduction temperature. At 250 °C (Fig. 3d), Sn existed solely as Sn^{4+} and Sn^{n+} (where $n = 2$ or 4). After reduction at 540 °C (Fig. 3e), a mixed valence state comprising Sn^0 , Sn^{2+} , and Sn^{4+} appeared [19, 26, 48]. Table S3 shows that Sn^0 accounted for 10.9% of the total Sn content [49]. Sn^{2+} is partially anchored within the zeolite framework via two Si-O-Sn bonds, providing binding sites for Pt particles and enabling their localization [26]. Meanwhile, part of the Sn^0 diffused into Pt particles, forming a Pt-Sn bimetallic phase. When the temperature was raised to 650 °C (Fig. 3), Sn^0 content further increased to 14.96%, indicating more extensive Sn-Pt interaction. However, HRTEM (Fig. 2j) revealed that Sn species migrated and covered Pt active sites. The XPS and TEM results suggest that Sn^{2+} species are associated with the stabilization of Pt particles, while a moderate amount of Sn^0 facilitates the generation of Pt-Sn interfacial interactions without inducing excessive Sn migration in Pt/Sn- β at 540 °C. These results suggest that metal-support interactions were well balanced at this reduction temperature.

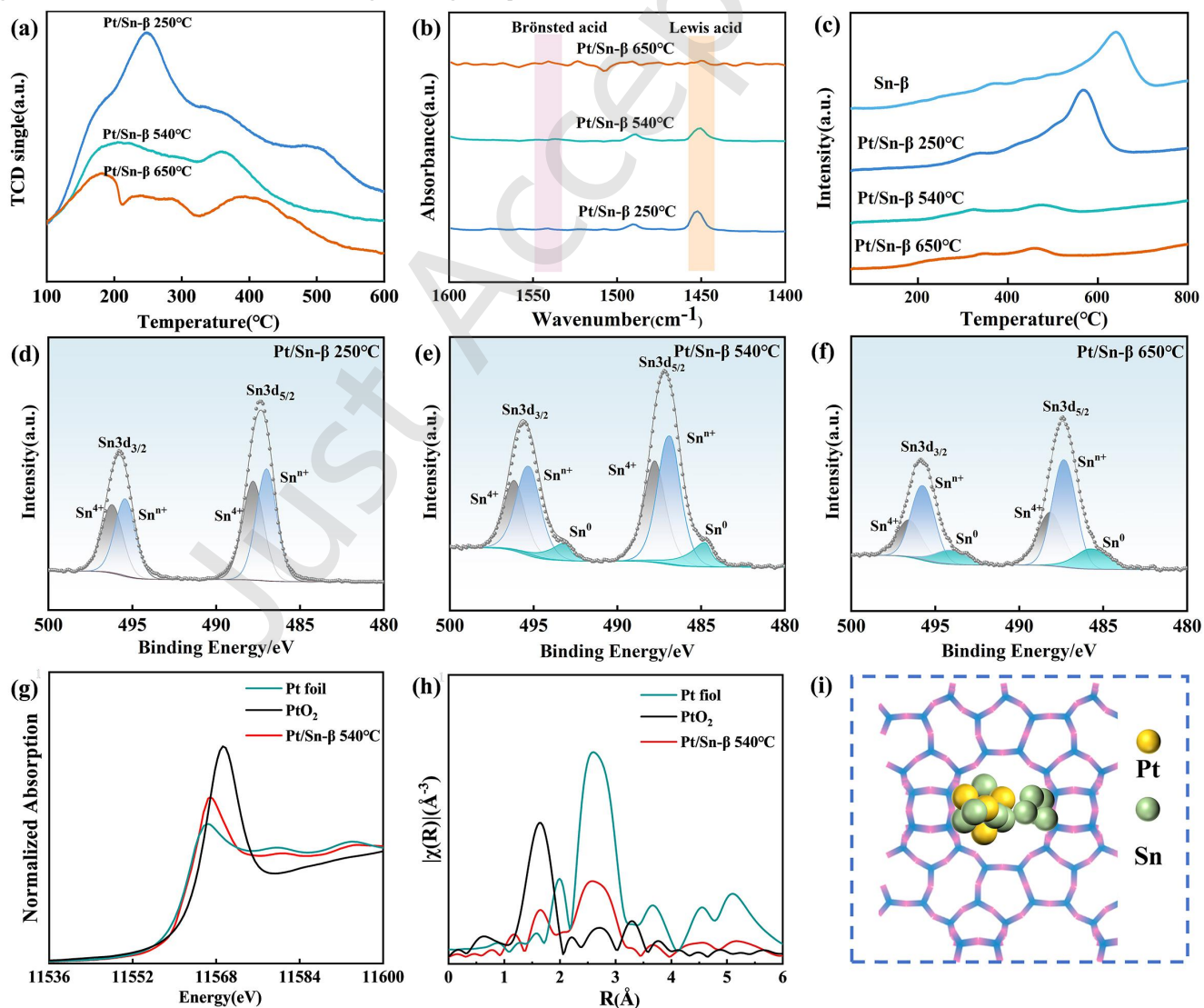


Fig. 3. (a) NH_3 -TPD profiles and (b) Py-IR spectra of the catalysts reduced at different temperatures (c) H_2 -TPR profiles and (d-f) XPS spectra of Sn 3d at different reduction temperatures (g) Pt $L_{3\text{-edge}}$ XANES spectra and (h) Fourier-transformed Pt $L_{3\text{-edge}}$ EXAFS spectra in R space of Pt/Sn- β 540°C, (i)

Pt foil, and PtO₂ (i) Schematic illustration of the Pt/Sn- β 540 °C catalyst structure.

The local coordination environment of Pt in Pt/Sn- β 540 °C was investigated by synchrotron-based Pt L₃-edge X-ray absorption spectroscopy. As shown in Fig. 3g, h, the Pt species exhibited a metallic coordination environment similar to that of Pt foil. EXAFS fitting (Table S4) gave Pt-Pt and Pt-Sn coordination numbers of 7.85 and 4.31, respectively, confirming the presence of direct Pt-Sn coordination. The wavelet-transform results in Fig. S13 further show that Pt/Sn- β 540 °C exhibits a strong high-K scattering feature similar to Pt foil, together with a weak low-K Pt-O contribution. These results confirm that Pt is predominantly present in a metallic environment, with a small fraction of oxygen-coordinated Pt, and that Sn enters the first coordination shell of Pt to form a bimetallic Pt-Sn architecture. Such a structure can be attributed to the intermediate reduction temperature of 540 °C, at which partially reduced metallic Sn species, whose bulk melting point is well below the reduction temperature, may exhibit enhanced mobility and migrate toward Pt [23,30], while zeolite confinement and framework-associated Sn suppress excessive aggregation, thereby favoring the formation of uniformly dispersed Pt-Sn bimetallic species.

Based on the combined structural characterizations including XRD, HRTEM, XPS, and EXAFS analyses, Fig. 3i illustrates the proposed structure of Pt/Sn- β 540 °C. The dominant structure is composed of highly dispersed Pt-Sn interfacial species with Pt-Sn coordination, while a small fraction of Sn species remains as Sn-rich particles.

3.3. Catalytic performance

Fig. 4a shows the effect of reduction temperature on the formation rate of mono-dodecene over the Pt/Sn- β catalyst. For the catalyst reduced at 250 °C, the initial formation rate was relatively low, reaching 0.00137 mol g_{Pt}⁻¹ s⁻¹ after 1 h of reaction. However, under the reaction conditions of 470 °C in an H₂ atmosphere, the formation rate gradually increased to 0.00170 mol g_{Pt}⁻¹ s⁻¹ as the reaction proceeded. This result indicates that an in situ activation process occurs during the reaction, which promotes the evolution of Sn valence states and optimizes Sn-Pt interactions. Upon reduction at 540 °C, the formation rate significantly improved to 0.00174 mol g_{Pt}⁻¹ s⁻¹ and remained stable throughout the reaction, suggesting that the catalyst structure was well optimized and that stable active sites were formed. In contrast, further increasing the reduction temperature to 650 °C led to complete catalyst deactivation, with the formation rate decreasing to zero. This deactivation is mainly attributed to severe Sn migration, which covers Pt active sites and induces pronounced structural degradation at high temperature. The Pt/Sn- β catalyst reduced at 540 °C exhibited excellent product selectivity and stable conversion (Fig. 4b). The initial conversion of n-dodecane reached 26.54% and gradually decreased to 22.12% during the reaction. The selectivity toward linear mono-dodecene remained at around 89%. The remaining products, grouped as “others”, mainly included dienes, aromatic products, and other minor byproducts. This high mono-dodecene selectivity demonstrates the high product specificity of Pt/Sn- β and its ability to suppress side reactions. Although the reaction conditions differed among the reported catalysts, the

comparison in Table S6 shows that Pt/Sn- β achieved a competitive mono-dodecene yield of 19.8%, providing a favorable balance between conversion and selectivity.

To further clarify the confinement and stabilization effects of the Sn- β support, SBA-15-supported samples were prepared as references. The small-angle and wide-angle XRD patterns are shown in Fig. S14a and b, respectively. Crystalline SnO₂ reflections were observed for Sn-SBA-15 in the wide-angle XRD pattern, reflecting the aggregation of Sn species on the mesoporous silica support. The N₂ adsorption-desorption isotherms and pore-size distributions (Fig. S14c and d), together with the textural data in Table S5, confirm that Pt/Sn-SBA-15 retained a predominantly mesoporous structure, with a mesopore volume of 1.153 cm³ g⁻¹. Nevertheless, its initial n-dodecane conversion was only approximately 3% and decreased rapidly, showing that open mesopores alone are insufficient to stabilize highly dispersed Pt-Sn species. This comparison highlights the additional anchoring and stabilization provided by the hierarchical pores and defect sites of Sn- β .

Fig. 4c compares the dehydrogenation performances of Pt/Sn- β and Pt/SnO₂- β prepared with different Sn sources, thereby revealing the effect of Sn speciation on catalytic behavior. In the Pt/SnO₂- β catalyst, Sn species mainly existed as SnO₂ before reduction, as indicated by the UV peak at 300 nm in Fig. S4. Without the confinement effect of the β -zeolite framework, Sn species are difficult to disperse uniformly after reduction, making it difficult to form a well-defined Pt-Sn interface in the Pt/SnO₂- β catalyst. Although the overall conversion remained relatively high, the selectivity toward the target product was limited, indicating that the chemical state and dispersion of Sn species play a critical role in regulating Pt-Sn interfacial structures and catalytic selectivity.

To elucidate the catalytically active sites for dodecane dehydrogenation, Fig. 4d shows the catalytic performance comparison among β , Sn- β , Pt/ β , and Pt/Sn- β . The conversions of β zeolite and Sn- β were both below 5% with no target product formation, indicating that relying solely on the zeolite framework or Sn introduction is insufficient to drive the reaction. After Pt loading, the conversion of Pt/ β increased to 52%, but the selectivity was only 40%, suggesting that Pt serves as an active center for dehydrogenation and effectively initiates the reaction, yet a single metal site alone cannot achieve high selectivity for the target reaction. With further Sn introduction, the Pt/Sn- β catalyst showed a slight decrease in conversion, but target-product selectivity increased to 89.6%. Sn incorporation forms Pt-Sn metallic particles, and support-anchored Sn stabilizes Pt active centers to suppress side reactions and enhance target selectivity.

Fig. 4e presents a schematic illustration of catalyst states under different reduction temperatures. As corroborated by this schematic and complementary characterizations, the Pt/Sn- β catalyst reduced at 250 °C exhibited no detectable crystalline phase of metallic Sn (Fig. 1a and 3d). The incomplete reduction of framework Sn resulted in insufficient Pt-Sn interfacial anchoring, leading to poor Pt dispersion and low selectivity. By contrast, excessive

reduction at 650 °C induced severe Sn migration and particle coarsening, which covered or buried the Pt active sites, causing catalyst deactivation. At the optimal temperature of 540 °C, multiple characterizations revealed that moderate reduction enabled Sn^{2+} to anchor at the support-Pt interface via Si–O–Sn bonds, while Sn formed ultrafine intermetallic

compounds with Pt. Meanwhile, the microporous β framework, secondary porosity, and defect sites provided confinement and anchoring effects for the ultrafine Pt-Sn species. These features suppressed metal migration and aggregation and promoted the isolation of adjacent Pt sites, thereby enhancing olefin selectivity and stability.

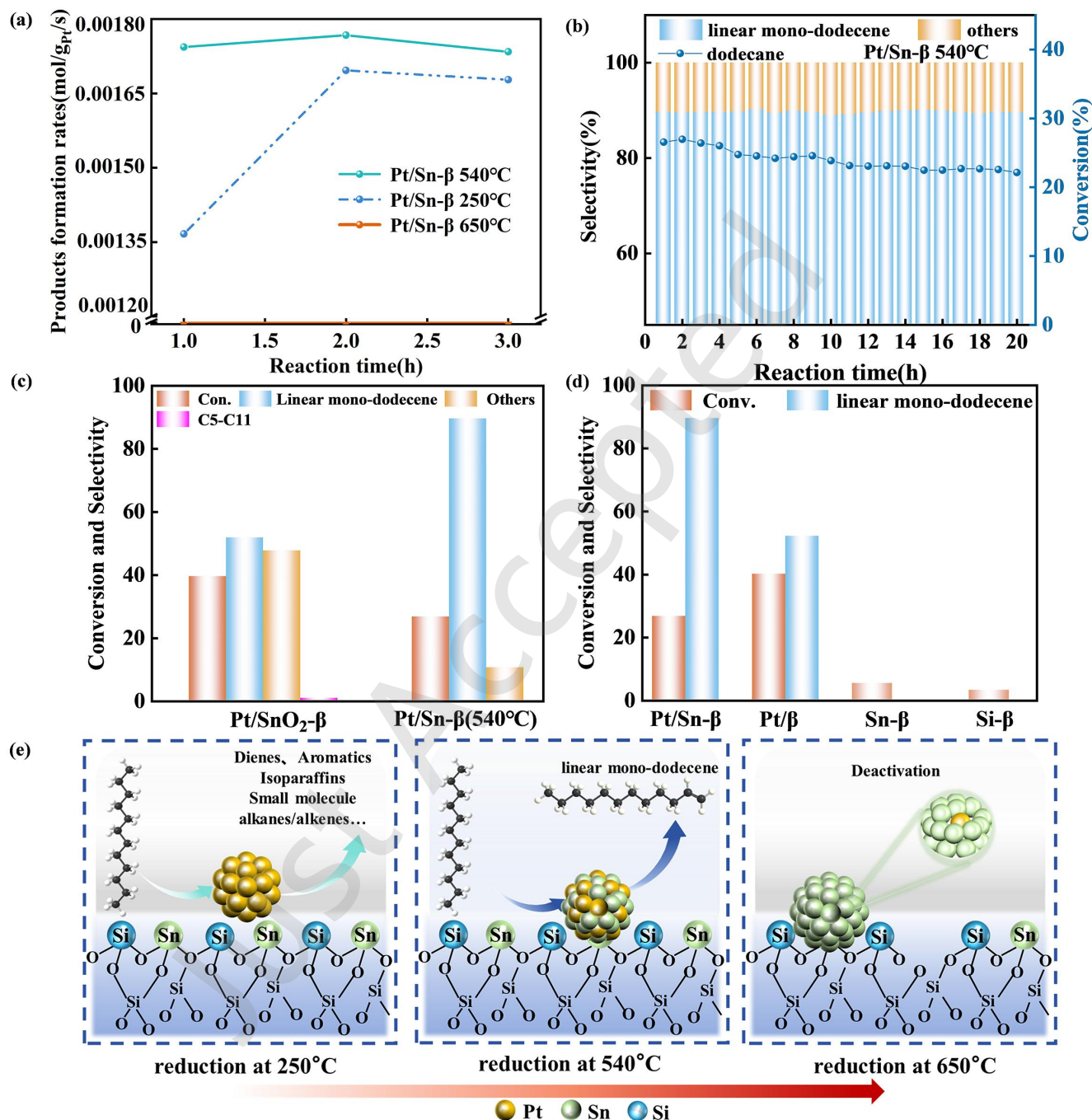


Fig. 4. (a) Product formation rates of Pt/Sn- β catalysts reduced at different temperatures, (b) Catalytic performance of the catalyst reduced at 540 °C for 20 h, (c) Comparison of catalytic results between Pt/SnO₂- β and Pt/Sn- β catalysts, (d) Comparison of catalytic performance over Pt/Sn- β , Pt/ β , Sn- β , and β catalysts, (e) Schematic diagram of particle distribution at different temperatures.

3.4. Dehydrogenation mechanism

In situ DRIFTS spectra of Si- β (a), Pt/ β (b), Sn- β (c) and Pt/Sn- β (d) were collected using a long-chain alkane as the probe molecule, as shown in Fig. 5. The comparative spectra of different catalysts recorded at reaction temperature and room temperature are presented in Fig. 5e and f, respectively. This analysis was performed to investigate the role of Pt-Sn interfacial sites in long-chain alkane activation,

intermediate evolution, and coke suppression. The removal of framework Al from β zeolite created abundant unoccupied T-sites, resulting in a high density of silanol defect sites (Si-OH, 3750-3500 cm^{-1}) in Pt/ β and Si- β [50]. The bands in the 2800-3000 cm^{-1} region correspond to the $\nu(\text{C-H})$ stretching vibrations of adsorbed alkane species. As the reaction temperature increased, the adsorbed alkanes were progressively activated and converted into olefin

intermediates/products, while excessive accumulation or secondary conversion of olefin species could lead to coke-related carbonaceous deposits [51, 52]. FTIR spectroscopy further revealed an infrared vibration at 1640 cm^{-1} corresponding to $\nu(\text{C}=\text{C})$ (Fig. S15), confirming dodecene formation on the Pt/Sn- β catalyst. The bands at 1272 cm^{-1} over Pt/ β and 1265 cm^{-1} over Pt/Sn- β are assigned to the CH_2 twisting vibration and/or C-C skeletal vibration of adsorbed alkane species [53]. This band was very weak over Si- β , indicating limited alkane adsorption/activation ability. The red shift observed on Pt/Sn- β suggests that Sn introduction modulates the electronic properties of Pt and strengthens the interaction between alkane molecules and Pt-Sn bimetallic sites.

Compared with Pt/ β , the Pt-H stretching band on Pt/Sn- β shifted from 1949 to 1955 cm^{-1} and became much weaker [54]. This blue shift indicates a modified electronic environment of Pt and a strengthened Pt-H bond, while the decreased intensity suggests a lower coverage of adsorbed H species due to the geometric dilution of Pt sites by Sn. These effects are beneficial for regulating hydrogen availability and

promoting olefin desorption [37]. In contrast, the Sn-H band observed on Sn- β indicates that Sn sites can adsorb hydrogen to some extent, but Sn-H species are less effective than Pt-H species in hydrogen migration and dehydrogenation. Sn- β exhibited a distinct band assigned to strongly adsorbed olefin-derived intermediates, together with a carbon deposition band at 1585 cm^{-1} [54]. Si- β also showed a pronounced carbon deposition band at 1585 cm^{-1} , likely due to side reactions such as cracking, oligomerization, and polymerization induced by surface defect sites. In contrast, Pt/Sn- β showed no obvious olefin intermediate band and an almost negligible carbon deposition band, indicating that the Pt-Sn interface suppresses the accumulation of olefin-derived intermediates and coke formation. Overall, this spectroscopic evidence provides mechanistic insight into the origin of Pt-Sn synergy: Sn geometrically dilutes Pt ensembles and electronically modulates adsorption strength, thereby promoting olefin desorption, suppressing carbon deposition, and enabling an effective balance between reactant activation and intermediate conversion [55, 56].

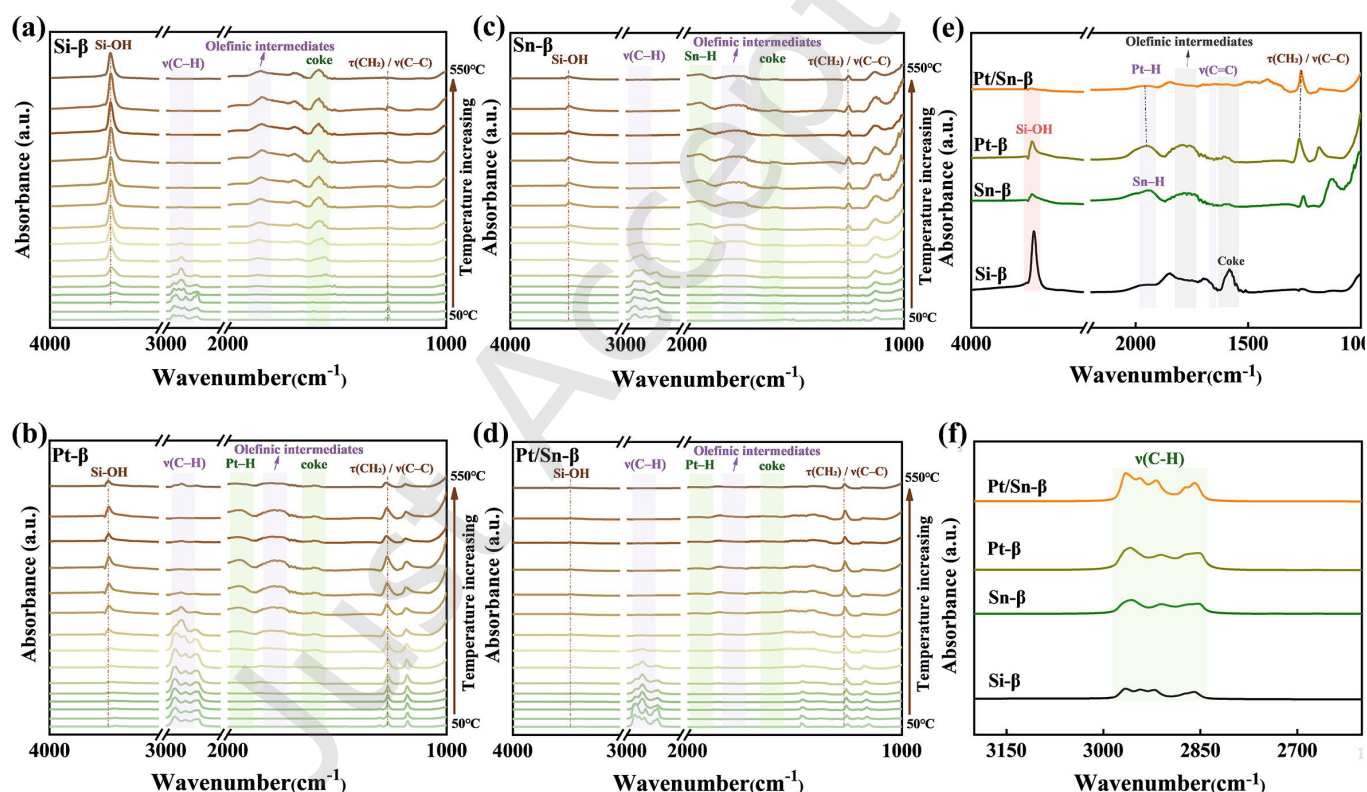


Fig. 5. *In situ* DRIFTS spectra of (a) Si- β , (b) Pt- β , (c) Sn- β , (d) Pt/Sn- β , and (e) Pt/Sn- β catalysts under H_2 atmosphere. Comparison of the *in situ* DRIFTS spectra of different catalysts under (e) reaction temperature and (f) room temperature conditions.

Based on catalyst structure analysis, *in situ* DRIFTS observations, and dehydrogenation activity evaluation, Fig. 6 illustrates the proposed dehydrogenation pathway. First, vaporized n-dodecane molecules diffuse to the catalyst surface and subsequently access the hierarchical pore environment of Sn- β (I). The microporous structure imposes a confinement effect on the diffusing molecules, while mesopores facilitate molecular transport. Comparison of the *in situ* DRIFTS spectrum of n-dodecane adsorbed on Pt/Sn- β 540°C in Fig. 5d-f with the conventional FT-IR spectrum of n-dodecane in Fig. S15 reveals a pronounced

change in the relative intensities of the C-H stretching bands. In the presence of the catalyst, the CH_3 -related bands become stronger than the CH_2 -related bands, indicating enhanced interaction between the terminal region of n-dodecane and the active sites. Combined with the confinement effect of the Sn- β pore structure, this spectral change suggests that n-dodecane preferentially approaches the Pt-Sn active sites through its terminal C1-C2 region, forming a constrained $\eta_2(\text{C1,C2})$ adsorption configuration. After reduction at 540°C , Pt and Sn interact to form highly dispersed Pt-Sn interfacial active sites stabilized by the Sn- β

framework. The adsorbed dodecane molecules then undergo C–H bond activation at these bimetallic sites, leading to the formation of surface dehydrogenation intermediates (II $\rightarrow$ III). The adjacent Sn species regulate the electronic and geometric environment of Pt sites, effectively isolating Pt ensembles and suppressing excessive dehydrogenation and side reactions. In contrast, Pt/Sn- β 250°C contains abundant strongly adsorbing acid sites, which promote undesired

cracking and isomerization reactions and consequently decrease the selectivity toward linear dodecenes. The olefin species generated during the reaction rapidly desorb from the catalyst surface, resulting in reduced secondary reactions and coke formation. Finally, surface hydrogen species recombine to release H₂, restoring the active sites and completing the dehydrogenation cycle.

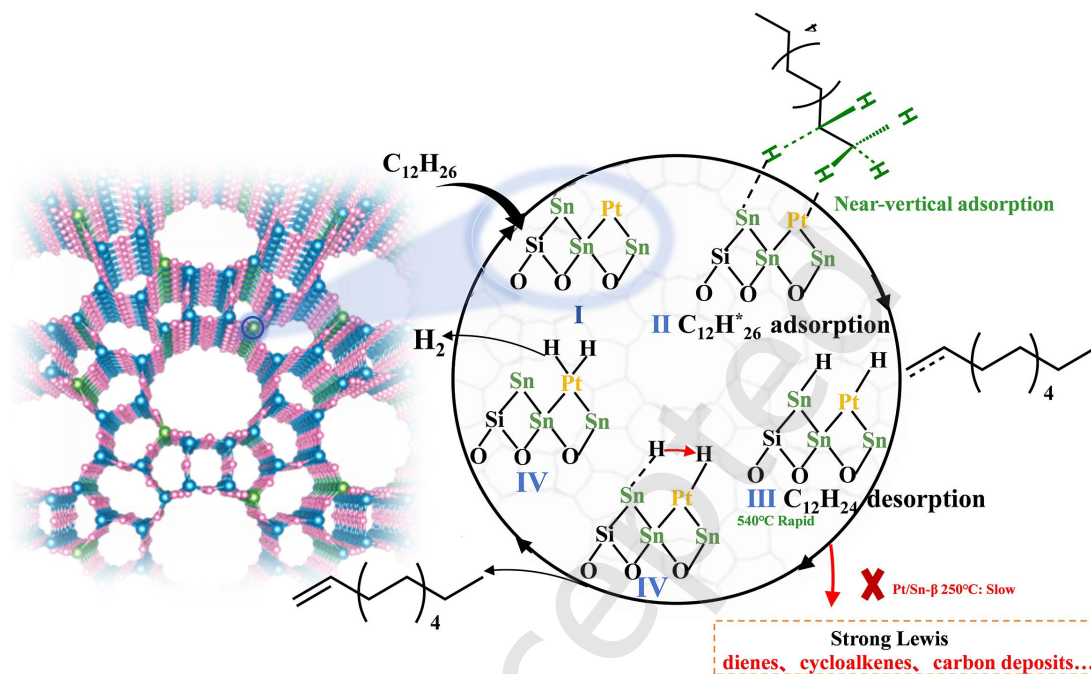


Fig. 6 Proposed dehydrogenation pathways of n-dodecane over Pt/Sn- β reduced at different temperatures.

4. Conclusion

In summary, an ultrafine Pt-Sn intermetallic catalyst is constructed in dealuminated β zeolite for long-chain alkane dehydrogenation. Reduction temperature precisely governs Sn speciation and the evolution of the Pt-Sn structure. At 540 °C, Sn²⁺ species are anchored at the Pt-zeolite interface while metallic Sn interacts directly with Pt to form an ultrafine Pt-Sn intermetallic structure. This intermetallic structure geometrically dilutes the Pt ensembles and favors olefin desorption, thereby suppressing secondary reactions such as C=C over-activation and C-C cleavage and contributing to the high selectivity for linear mono-olefins. The dealuminated β zeolite provides spatial confinement for ultrafine Pt-Sn species while eliminating acid-catalyzed side reactions. A clear reduction-temperature-structure-performance correlation is established, providing a general strategy for regulating Pt-Sn active sites for selective long-chain alkane dehydrogenation.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

The financial support by the National Natural Science Foundation (22478276, 22408221), and Shanxi Province Basic Research Program Joint Funding Project (Lu'an)

(202403011242003) are gratefully acknowledged.

Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Ying Qiu: Methodology, Investigation, Data curation, Writing – original draft. Jianchao Liu: Methodology, Formal analysis. Mingge Zhang: Investigation, Validation. Yu Liang: Supervision, Writing – review & editing. Lei Liu: Supervision, Funding acquisition, Writing – review & editing. Jinxiang Dong: Supervision.

Use of AI statement

None

References

- [1] Ren, Y.; Liao, Z. W.; Sun, J. Y.; Jiang, B. B.; Wang, J. D.; Yang, Y. R.; Wu, Q. Molecular reconstruction: Recent progress toward composition modeling of petroleum fractions. *Chem. Eng. J.* **2019**, 357, 761-775.
- [2] Bhasin, M. M.; McCain, J. H.; Vora, B. V.; Imai, T.; Pujadó, P. R. Dehydrogenation and oxydehydrogenation of paraffins to olefins. *Appl. Catal. A Gen.* **2001**, 221, 397-419.
- [3] Lin, J.; Yang, J.; Li, T.; Zhao, S.; Huang, W. H.; Chen, C. L.; Zhao, Y.; Liu, S.; Gu, L.; Yang, L.; Qiu, Y.; Chen, G. Surface structure engineering of PtCu clusters enhances the performance of propane dehydrogenation. *Nano Res.* **2025**, 18, 94907357.
- [4] Vora, B. V. Development of dehydrogenation catalysts and processes. *Top. Catal.* **2012**, 55, 1297-1308.

- [5] Yu, P.; Cui, M. T.; Li, Q. Y.; Wang, D.; Wang, Z.; Li, M. S.; Li, X. B. Active, selective and stable Pt/Fe-silicalite-1 catalyst for dehydrogenation of n-dodecane to linear mono-dodecene. *Appl. Catal. A Gen.* **2020**, 608, 117860.
- [6] He, S. B.; Sun, C. L.; Yang, X.; Wang, B.; Dai, X. H.; Bai, Z. W. Characterization of coke deposited on spent catalysts for long-chain-paraffin dehydrogenation. *Chem. Eng. J.* **2010**, 163, 389-394.
- [7] Torres Martí, F.; Mathieu, Y.; Corma, A. Cracking of hydrotreated waste fats and oils over zeolites for renewable propene production. Part II: Cracking of Hydrotreated & isomerized paraffinic products derived from the hydroprocessed esters and fatty acids (HEFA) process. *Appl. Catal. B Environ. Energy* **2026**, 381, 125884.
- [8] Shi, L.; Deng, G. M.; Li, W. C.; Miao, S.; Wang, Q. N.; Zhang, W. P.; Lu, A. H. Al₂O₃ nanosheets rich in pentacoordinate Al³⁺ ions stabilize Pt-Sn clusters for propane dehydrogenation. *Angew. Chem. Int. Ed.* **2015**, 54, 13994-13998.
- [9] He, S. B.; Wang, B.; Dai, X. H.; Sun, C. L.; Bai, Z. W.; Wang, X.; Guo, Q. Industrial development of long chain paraffin (n-C₁₀⁰-C₁₃⁰) dehydrogenation catalysts and the deactivation characterization. *Chem. Eng. J.* **2015**, 275, 298-304.
- [10] Vicerich, M. A.; Benitez, V. M.; Especel, C.; Epron, F.; Pieck, C. L. Influence of iridium content on the behavior of Pt-Ir/Al₂O₃ and Pt-Ir/TiO₂ catalysts for selective ring opening of naphthenes. *Appl. Catal. A Gen.* **2013**, 453, 167-174.
- [11] Xie, L. J.; Chai, Y. C.; Sun, L. L.; Dai, W. L.; Wu, G. J.; Guan, N. J.; Li, L. D. Optimizing zeolite-stabilized Pt-Zn catalysts for propane dehydrogenation. *J. Energy Chem.* **2021**, 57, 92-98.
- [12] Deng, L. D.; Wang, J. W.; Wu, Z. K.; Liu, C. H.; Qing, L.; Liu, X. W.; Xu, J.; Zhou, Z. J.; Xu, M. H. Effects of second metals (M = Fe, Cu, Ga, In, Sn) on the geometric and electronic properties of platinum for the direct dehydrogenation of propane. *J. Alloys Compd.* **2022**, 909, 164820.
- [13] Zhang, T. T.; Pei, C. L.; Sun, G. D.; Chen, S.; Zhao, Z. J.; Sun, S. J.; Lu, Z. P.; Xu, Y. Y.; Gong, J. L. Synergistic mechanism of platinum GaOx catalysts for propane dehydrogenation. *Angew. Chem. Int. Ed.* **2022**, 61, e202201453.
- [14] Wu, K.; Fang, Z.; Peng, C.; Zhang, Y.; Jiang, B.; Kang, Y.; Chen, Z.; Ye, M.; Wu, Y.; Wei, X.; Liu, S.; Li, S.; Zhang, J. Cu1-B dual-active sites catalysts for the efficient dehydrogenative coupling and CO₂ electroreduction. *Nano Res.* **2023**, 16, 4582-4588.
- [15] Xu, Z. K.; Gao, M. B.; Wei, Y.; Yue, Y. Y.; Bai, Z. S.; Yuan, P.; Fornasiero, P.; Basset, J. M.; Mei, B. B.; Liu, Z. M.; Zhu, H. B.; Ye, M.; Bao, X. J. Pt migration-lockup in zeolite for stable propane dehydrogenation catalyst. *Nature* **2025**, 643, 691-698.
- [16] Nykänen, L.; Honkala, K. Density functional theory study on propane and propene adsorption on Pt(111) and PtSn alloy surfaces. *J. Phys. Chem. C* **2011**, 115, 9578-9586.
- [17] Latimer, A. A.; Kulkarni, A. R.; Aljama, H.; Montoya, J. H.; Yoo, J. S.; Tsai, C.; Abild-Pedersen, F.; Studt, F.; Nørskov, J. K. Understanding trends in C-H bond activation in heterogeneous catalysis. *Nat. Mater.* **2017**, 16, 225-229.
- [18] Chen, K.; Bell, A. T.; Iglesia, E. The relationship between the electronic and redox properties of dispersed metal oxides and their turnover rates in oxidative dehydrogenation reactions. *J. Catal.* **2002**, 209, 35-42.
- [19] Wu, B.; Shi, Y. C.; Zhang, J. M.; Wang, Z. X.; Sun, S. H.; Wang, L.; Huang, H.; Zhang, L. L.; Wu, Y. L. Stabilizing ultra-small bimetallic PtSn clusters within S-1 crystals for effective propane dehydrogenation with low Pt loading. *Chem. Eng. J.* **2024**, 498, 155205.
- [20] Lee, S.; Park, Y.; Choi, M. Cooperative interplay of micropores/mesopores of hierarchical zeolite in chemical production. *ACS Catal.* **2024**, 14, 2031-2048.
- [21] Miao, C. X.; Liu, M.; Tan, S. D.; Zhang, G. K.; Chu, S. Q.; Song, S. J.; Zhang, Q. Y.; Yu, J. J.; Jiang, G. Y.; Song, W. Y.; He, Q.; Luo, W. H.; Wu, Z. J. Pt-Sn nanoalloys on Sn-Beta zeolite for efficient propane dehydrogenation. *Microporous Mesoporous Mater.* **2023**, 361, 112736.
- [22] Chen, C.; Hu, Z. P.; Ren, J. T.; Zhang, S. M.; Wang, Z.; Yuan, Y. Y. ZnO nanoclusters supported on dealuminated zeolite β as a novel catalyst for direct dehydrogenation of propane to propylene. *ChemCatChem* **2019**, 11, 868-877.
- [23] Tang, B.; Dai, W. L.; Wu, G. J.; Guan, N. J.; Li, L. D.; Hunger, M. Improved postsynthesis strategy to Sn-Beta zeolites as Lewis acid catalysts for the ring-opening hydration of epoxides. *ACS Catal.* **2014**, 4, 2801-2810.
- [24] Xie, D. New insight from an old concept for zeolites. *Science* **2021**, 373, 28.
- [25] Yi, X. F.; Liu, K. Y.; Chen, W.; Li, J. J.; Xu, S. T.; Li, C. B.; Xiao, Y.; Liu, H. C.; Guo, X. W.; Liu, S. B.; Zheng, A. M. Origin and structural characteristics of tri-coordinated extra-framework aluminum species in dealuminated zeolites. *J. Am. Chem. Soc.* **2018**, 140, 10764-10774.
- [26] Xu, Z. K.; Yue, Y. Y.; Bao, X. J.; Xie, Z. L.; Zhu, H. B. Propane dehydrogenation over Pt clusters localized at the Sn single-site in zeolite framework. *ACS Catal.* **2020**, 10, 818-828.
- [27] Joshi, H.; Ochoa-Hernández, C.; Nürenberg, E.; Kang, L.; Wang, F. R.; Weidenthaler, C.; Schmidt, W.; Schüth, F. Insights into the mechanochemical synthesis of Sn-β: Solid-state metal incorporation in beta zeolite. *Microporous Mesoporous Mater.* **2020**, 309, 110566.
- [28] Lu, C.; Zhou, W. T.; Zhang, X.; Feng, N. J.; Wan, H.; Guan, G. F. Pinpointing the critical threshold between dealumination and structural collapse in Beta zeolite for efficient toluene capture under humid environment. *Sep. Purif. Technol.* **2026**, 381, 135597.
- [29] Lu, S. C.; Xue, W. J.; Wang, H.; Liu, Q. L.; Han, R.; Mei, D. H. A surface-induced coating strategy for constructing hydrophobic zeolite composite to enhance the toluene adsorption in humid environment. *Chem. Eng. J.* **2023**, 471, 144570.
- [30] Zhao, X. P.; Zhou, Z. M.; Luo, H.; Zhang, Y. F.; Liu, W.; Miao, G.; Zhu, L. J.; Kong, L. Z.; Li, S. G.; Sun, Y. H. γ-Valerolactone-introduced controlled-isomerization of glucose for lactic acid production over an Sn-Beta catalyst. *Green Chem.* **2021**, 23, 2634-2639.
- [31] Jarrin, T.; Bruin, T.; Chizallet, C. Impact of point defects, external surface sites, and Si/Al ratio on Al-O bonds hydrolysis kinetics at the initiation of faujasite dealumination. *ACS Catal.* **2024**, 14, 1639-1652.
- [32] Wang, Y. S.; Hu, Z. P.; Tian, W. W.; Gao, L. J.; Wang, Z.; Yuan, Z. Y. Framework-confined Sn in Si-beta stabilizing ultra-small Pt nanoclusters as direct propane dehydrogenation catalysts with high selectivity and stability. *Catal. Sci. Technol.* **2019**, 9, 6993-7002.
- [33] Ma, Y.; Chen, X.; Guan, Y. J.; Xu, H.; Zhang, J. W.; Jiang, J. G.; Chen, L.; Xue, T.; Xue, Q. S.; Wei, F.; Wu, P. Skeleton-Sn anchoring isolated Pt site to confine subnanometric clusters within *BEA topology. *J. Catal.* **2021**, 397, 44-57.
- [34] Wang, C.; Tissot, H.; Soldemo, M.; Lu, J.; Weissenrieder, J. Inverse single-site Fe1(OH)_x/Pt(111) model catalyst for preferential oxidation of CO in H₂. *Nano Res.* **2022**, 15, 709-715.
- [35] Wang, H.; Xiang, Z. X.; Zhang, X. Y.; Su, Z. P.; Chen, R.; Chen, T. H. Rare-earth-modified magnesium aluminate spinel-supported PtSn nanoparticles for propane dehydrogenation. *ACS Catal.* **2025**, 15, 14682-14692.
- [36] Lee, B. S.; Lin, H. P.; Chan, J. C. C.; Wang, W. C.; Hung, P. H.; Tsai, Y. H.; Lee, Y. L. A novel sol-gel-derived calcium silicate cement with short setting time for application in endodontic repair of perforations. *Int. J. Nanomedicine* **2018**, 13, 261-271.
- [37] Xue, Q. Q.; Lim, K. H.; Huang, T. Y.; Cheng, S. W.; Yan, B. H.; Yin, Z. Y.; Wang, Y. J.; Luo, G. S.; Kawi, S. Tailoring Pt-Sn coordination triggered SnO_x-modified Pt cluster for propane dehydrogenation. *ACS Catal.* **2025**, 15, 15067-15080.
- [38] Loricera, C. V.; Navarro Yerga, R.; Barrio, L.; Pawelec, B.; Fierro, J. L. G. Synergistic effect in vapor phase hydrodeoxygenation on USY zeolite supported Ir-Pt catalyst: Role of pentacoordinated Al³⁺ ions. *Ind. Eng. Chem. Res.* **2021**, 60, 18707-18721.
- [39] Javed, M.; Cheng, S.; Zhang, G.; Amoo, C. C.; Wang, J.; Lu, P.; Lu, C.; Xing, C.; Sun, J.; Tsubaki, N. A facile solvent-free synthesis strategy for Co-imbedded zeolite-based Fischer-Tropsch catalysts for direct gasoline production. *Chin. J. Catal.* **2020**, 41, 604-612.
- [40] Schroeder, C.; Hansen, M. R.; Koller, H. Ultrastabilization of zeolite Y transforms Brønsted-Brønsted acid pairs into Brønsted-Lewis acid pairs. *Angew. Chem. Int. Ed.* **2018**, 57, 14281-14285.

- [41] Yue, X.; Hou, Y.; Xie, L.; Han, F.; Zhang, Z.; Guan, Q.; Li, W. In-situ encapsulation of Pt and acid-site engineering in hierarchical SAPO-11 for enhanced isomerization-cracking and anti-coking in sustainable aviation fuel production. *Green Energy Environ.* **2026**, 11, 1362-1372.
- [42] Šivec, R.; Pomeroy, B.; Huš, M.; Likozar, B.; Grilc, M. Modelling of transport, adsorption and surface reaction kinetics on Ni, Pd and Ru metallic/acidic catalyst sites during hydrodeoxygenation of furfural. *Chem. Eng. J.* **2024**, 483, 149284.
- [43] Dabbawala, A. A.; Al Maksoud, W.; Abou-Hamad, E.; Charisiou, N. D.; Constantinou, A.; Harkou, E.; Latsiou, A. I.; AlKhoori, S.; Hinder, S. J.; Baker, M. A.; Anjum, D. H.; Kobayashi, Y.; Goula, M. A.; Polychronopoulou, K. Tuning of the acid sites in the zeolite-alumina composite Ni catalysts and their impact on the palm oil hydrodeoxygenation reaction. *Chem. Eng. J.* **2024**, 493, 152351.
- [44] Liu, J.; Yue, Y. Y.; Liu, H. Y.; Da, Z. J.; Liu, C. C.; Ma, A.; Rong, J. F.; Su, D. S.; Bao, X. J.; Zheng, H. D. Origin of the robust catalytic performance of nanodiamond-graphene-supported Pt nanoparticles used in the propane dehydrogenation reaction. *ACS Catal.* **2017**, 7, 3349-3355.
- [45] Armendáriz, H.; Guzmán, A.; Toledo, J. A.; Llanos, M. E.; Vázquez, A.; Aguilar-Ríos, G. Isopentane dehydrogenation on Pt-Sn catalysts supported on Al-Mg-O mixed oxides: Effect of Al/Mg atomic ratio. *Appl. Catal. A Gen.* **2001**, 211, 69-80.
- [46] Aguilar-Ríos, G.; Valenzuela, M.; Salas, P.; Armendáriz, H.; Bosch, P.; Del Toro, G.; Silva, R.; Bertín, V.; Castillo, S.; Ramírez-Solís, A.; Schifter, I. Hydrogen interactions and catalytic properties of platinum-tin supported on zinc aluminate. *Appl. Catal. A Gen.* **1995**, 127, 65-75.
- [47] Feng, J.; Zhang, M.; Yang, Y. Dehydrogenation of propane on Pt or PtSn catalysts with Al₂O₃ or SBA-15 support. *Chin. J. Chem. Eng.* **2014**, 22, 1232-1236.
- [48] Yue, Y.; Fu, J.; Wang, C.; Yuan, P.; Bao, X.; Xie, Z.; Basset, J. M.; Zhu, H. Propane dehydrogenation catalyzed by single Lewis acid site in Sn-Beta zeolite. *J. Catal.* **2021**, 395, 155-167.
- [49] Yang, M. L.; Zhu, Y. A.; Zhou, X. G.; Sui, Z. J.; Chen, D. First-principles calculations of propane dehydrogenation over PtSn catalysts. *ACS Catal.* **2012**, 2, 1247-1258.
- [50] Wachs, I. E. Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts. *Catal. Today* **1996**, 27, 437-455.
- [51] Resini, C.; Montanari, T.; Busca, G.; Jehng, J. M.; Wachs, I. E. Comparison of alcohol and alkane oxidative dehydrogenation reactions over supported vanadium oxide catalysts: In situ infrared, Raman and UV-vis spectroscopic studies of surface alkoxide intermediates and of their surface chemistry. *Catal. Today* **2005**, 99, 105-114.
- [52] Li, X. Y.; Lin, J.; Li, L.; Huang, Y. K.; Pan, X. L.; Collins, S. E.; Ren, Y. J.; Su, Y.; Kang, L. L.; Liu, X. Y.; Zhou, Y. L.; Wang, H.; Wang, A. Q.; Qiao, B. T.; Wang, X. D.; Zhang, T. Controlling CO₂ hydrogenation selectivity by metal-supported electron transfer. *Angew. Chem. Int. Ed.* **2020**, 59, 19983-19989.
- [53] Yamazoe, S.; Yamamoto, A.; Hosokawa, S.; Fukuda, R.; Hara, K.; Nakamura, M.; Kamazawa, K.; Tsukuda, T.; Yoshida, H.; Tanaka, T. Identification of hydrogen species on Pt/Al₂O₃ by in situ inelastic neutron scattering and their reactivity with ethylene. *Catal. Sci. Technol.* **2021**, 11, 116-123.
- [54] Sun, L. H.; Li, Q. Y.; Xu, Y. S.; Xia, S. Y.; Xu, D.; Lin, X.; Xu, J.; Chen, J. S.; Li, G. D.; Li, X. H. Tunable hydrogen coverage on electron-deficient platinum nanoparticles for efficient hydrogenation reactions. *Nano Res.* **2023**, 16, 10648-10656.
- [55] Jiao, J. H.; Yang, Y.; Yuan, M. J.; Tang, X. Q.; Shi, M. F.; He, K.; Zhang, H. J.; Bi, Y. F.; Qin, Y. C.; Song, L. J. Coke deposition mechanisms of propane dehydrogenation on different sites of Al₂O₃ supported PtSn catalysts. *Chem. Synth.* **2025**, 5, 19.
- [56] Newmeyer, E. R.; Wang, Y.; Long, Z. A.; North, J. D.; Shi, Y. X.; Swearer, D. F. Plasmonic charge localization and C-H activation at single-atom sites in dilute copper platinum alloys. *J. Am. Chem. Soc.* **2025**, 147, 11789-11799.

Ultrafine Pt-Sn intermetallic catalyst constructed in β zeolite for long-chain alkane dehydrogenation

Ying Qiu¹, Jianchao Liu¹, Mingge Zhang¹, Yu Liang²✉, Lei Liu¹✉, and Jinxiang Dong¹

¹ Shanxi Key Laboratory of Chemical Product Engineering, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

² Shanxi Key Laboratory of Bioagent Utilization and Eco-Pesticide Innovation, College of Plant Protection, Shanxi Agricultural University, Taigu 030801, China

Supporting information to <https://doi.org/10.26599/NR.2026.94909180>

INFORMATION ABOUT ELECTRONIC SUPPLEMENTARY MATERIAL.

S1. Detailed synthesis procedure of catalysts:

Si- β : Commercial Al- β zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was treated with 13 M HNO_3 (liquid-to-solid ratio 20 mL/g) at stirring for 20 h to remove framework Al completely. The solid was filtered, washed with deionized water to neutral pH, and vacuum-dried at 353 K for 12 h to obtain dealuminated β zeolite (Si- β).

Sn- β and SnO_2 - β : Sn species were introduced via solid-state grinding followed by stepwise calcination. Si- β was ground with tin acetate ($\text{Sn}(\text{CH}_3\text{COO})_2$) or SnO_2 (Si/Sn = 15) to obtain precursors. The precursors were calcined at 823 K for 3 h under Ar to decompose tin species and facilitate Sn migration into the framework, followed by air calcination at 823 K for 3 h to remove organics and stabilize Sn species

Pt/Sn- β and Pt/ SnO_2 - β : Pt (from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and K (from KCl) were loaded onto Sn-modified supports by incipient wetness impregnation (0.5 wt% each). The samples were dried at 353 K for 12 h and calcined in air at 823 K for 2 h to obtain Pt/Sn- β and Pt/ SnO_2 - β .

S2. Detailed Information of Characterization Instruments

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Cu $\text{K}\alpha$ radiation ($\lambda = 0.1541$ nm, 40 kV, 30 mA) in the 2θ range of 5 – 80° (scan rate $2^\circ/\text{min}$).

Nitrogen physisorption isotherms were measured on a Micromeritics ASAP 2020 analyzer. Samples were degassed at 200°C (6.7×10^{-4} bar) for 6 h prior to analysis (77 K).

UV-vis diffuse reflectance spectra were recorded on a Lambda 650 spectrometer (PerkinElmer) equipped with an integrating sphere (190–900 nm, 1 nm step).

Chemisorption and temperature-programmed analyses were conducted on a Micromeritics AutoChem II 2920 (TCD). NH_3 temperature-programmed desorption (NH_3 -TPD) was used to determine acidity. H_2 temperature-programmed reduction (H_2 -TPR) was used to examine reducibility. H_2 pulse chemisorption was used to quantify metal dispersion.

Surface acidity was characterized by Fourier-transform infrared (FTIR) spectroscopy (Bruker INVENIO R). Framework structure was confirmed by transmission FTIR. Pyridine adsorption (Py-IR) was employed to quantify Brønsted and Lewis acid sites. Samples were pressed into 13 mm self-supporting wafers, pretreated at 300°C ($\sim 10^{-7}$ Pa) for 1 h, exposed to pyridine at 40°C for 3 min, and evacuated at 300°C . Acid site concentrations were calculated using Eqs. (1) and (2):

$$C_B(\text{mmol/g}) = 1.88A(B) \times R^2 / W \quad (1)$$

$$C_L(\text{mmol/g}) = 1.42A(L) \times R^2 / W \quad (2)$$

where $A(B)$ and $A(L)$ are the integrated absorbances of the Brønsted and Lewis acid bands, R is the wafer radius (cm), and W is the wafer mass (mg).

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi (monochromatic Al $\text{K}\alpha$, 1486.6 eV, 150 W). Survey and high-resolution scans were collected at pass energies of 100 and 50 eV, respectively ($P < 10^{-8}$ mbar). Binding energies were calibrated to the C 1s peak at 284.8 eV.

Pt $\text{L}_{3\text{-edge}}$ X-ray absorption fine structure (XAFS) measurements were performed at the BL14W beamline of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China) using a Si(111) crystal monochromator. The powder samples were loaded into aluminum sample holders and sealed with Kapton tape. The spectra were collected at room temperature using a four-channel silicon drift detector (SDD, Bruker 5040). The catalyst sample was measured in fluorescence mode, while Pt foil and PtO_2 reference samples were measured in transmission mode.

In situ H_2 adsorption diffuse reflectance infrared spectroscopy (H_2 -DRIFTS) was performed on a Bruker INVENIO FT-IR spectrometer. The sample was pretreated at 200°C (30 mL/min Ar) for 30 min, cooled to room temperature, exposed to 5% H_2/Ar (30 mL/min), and heated to 550°C with spectra recorded.

Tab. S1. Physicochemical properties of supports and catalysts

Sample	Si/Al	S _{BET} (m ² /g)	S _{ext} (m ² /g)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)
H-β	14.27	496.99	76.72	420.26	0.39	0.20	0.19
Si-β	>600 0	439.05	93.38	345.67	0.42	0.17	0.25
Sn-β	>600 0	422.52	91.42	331.10	0.37	0.16	0.21
Pt/Sn-β 250 °C	>600 0	365.66	82.62	283.04	0.34	0.13	0.17
Pt/Sn-β 540 °C	>600 0	364.68	76.20	288.47	0.37	0.14	0.23
Pt/Sn-β 650 °C	>600 0	346.06	65.79	280.27	0.29	0.13	0.16

Tab. S2. Acid site concentrations of the support and catalysts

Sample	Weak acid sites[umol/g] ^a	Medium acid sites[umol/g] ^a	Strong acid [umol/g] ^a	Brønsted acidity[mmol/g] ^b	Lewis acidity ^b [mmol/g] ^b
H-β	4147	163.52	/	0.201	0.1799
Sn-β	2009	/	782.7	n.d.	0.0133
Pt/Sn-β 250 °C	1106	/	1319	n.d.	0.041
Pt/Sn-β 540 °C	381.44	718.28	/	n.d.	0.057
Pt/Sn-β 650 °C	244.22	133	336	n.d.	0.003

^a Acid-site concentrations determined by deconvolution of the NH₃-TPD profiles.^b Brønsted and Lewis acid concentrations determined by pyridine-adsorbed FTIR spectroscopy.

n.d.: not detected.

Tab. S3. XPS Sn 3d_{5/2} fitting parameters for Sn⁰, Sn²⁺, and Sn⁴⁺ species.

Sample	Sn ⁴⁺ Area (%) / BE(eV)	Sn ²⁺ Area (%) / BE(eV)	Sn ⁰ Area (%) / BE(eV)
Pt/Sn-β 250 °C	47.95/487.8	52.41/487	/
Pt/Sn-β 540 °C	38.68/487.8	50.42/486.9	10.9/484.8
Pt/Sn-β 650 °C	30.58/488.2	54.46/487.3	14.96/485.7

Tab. S4. Pt L₃-edge EXAFS fitting parameters for Pt foil and Pt/Sn-β-540 °C.

Samples	Paths	R(Å)	CN	δ ² (×100 Å ²)	ΔE ₀ (eV)	R-factor (%)
Pt foil	Pt-Pt	2.75	12	0.45	6.46	0.0011
Sample	Pt-Pt	2.74	7.85	0.76	8.89	0.0167
	Pt-Sn	2.92	4.31	3.9		

The amplitude reduction factor (S_0^2) was determined by fitting the Pt foil with the Pt-Pt coordination number fixed at 12 and was subsequently fixed during the fitting of the sample. R, bond distance; CN, coordination number; σ^2 , Debye-Waller factor; ΔE_0 , energy shift; R-factor, goodness of fit.

Tab. S5. Physicochemical properties of SBA-15 supports and catalysts

Sample	$S_{\text{BET}}(\text{m}^2/\text{g})$	$S_{\text{ext}}(\text{m}^2/\text{g})$	$S_{\text{micro}}(\text{m}^2/\text{g})$	$V_{\text{total}}(\text{cm}^3/\text{g})$	$V_{\text{micro}}(\text{cm}^3/\text{g})$	$V_{\text{meso}}(\text{cm}^3/\text{g})$
SBA-15	573.46	500.63	72.82	1.73	0.03	1.70
Sn-SBA-15	517.21	455.3	61.91	1.61	0.02	1.59
Pt/Sn-SBA-15	369.53	347.19	22.33	1.16	0.007	1.153

Tab. S6. The results of different catalysts in the dehydrogenation of long-chain alkanes

Catalyst	Ingredients	LHSVh ⁻¹	Pressure MPa	Temperature °C	Covn. %	Sel. %	Yield %	References
Pt-Sn-K-Mg/ γ -Al ₂ O ₃	n-C10-C13	20	0.14	460-500	11.6	94.1	10.9	[1]
Pt-Sn/SBA-15	C12	20	0.1	470	10	70	7	[2]
Pt-Sn-K/TiO ₂ -Al ₂ O ₃	n-C10-C13	20	0.14	453	22	87	19.14	[3]
Pt/Na-[Fe]-ZSM-5	C12	-	0.1	470	20	92.7	18.54	[4]
Pt/Fe-silicalite-1	C12	-	0.1	450	55	72	39.60	[5]
Pt/Sn- β	C12	12	0.1	470	22.12	89.5	19.8	This work ^a

^a Data obtained after 20 h on stream.

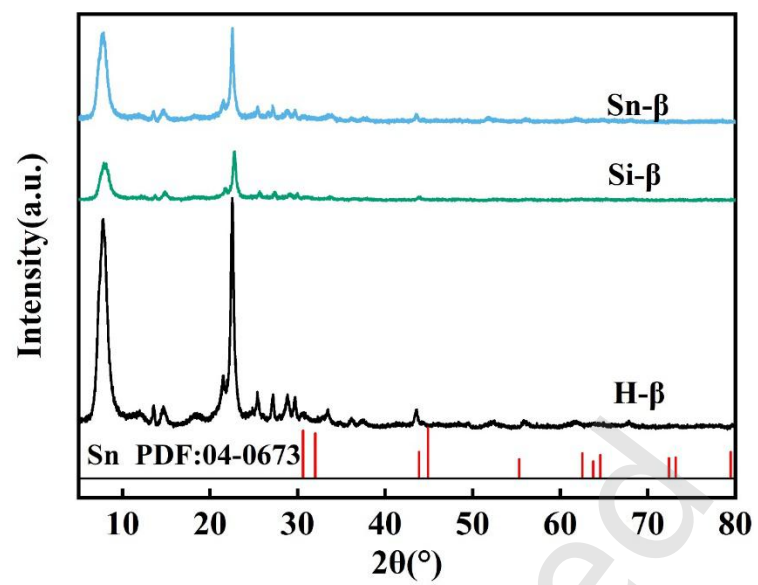


Fig. S1. XRD patterns of the H-β, Si-β, Sn-β.

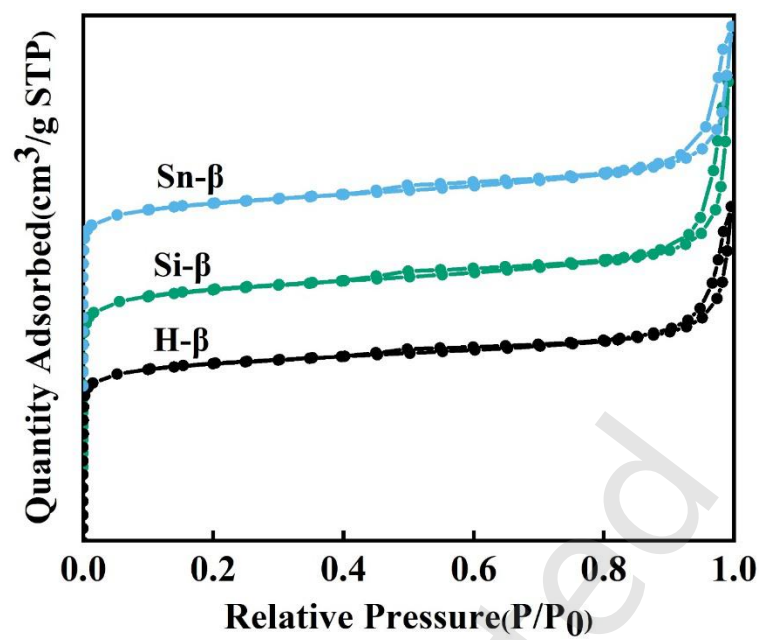


Fig. S2. N₂ adsorption-desorption isotherms of H-β, Si-β, and Sn-β.

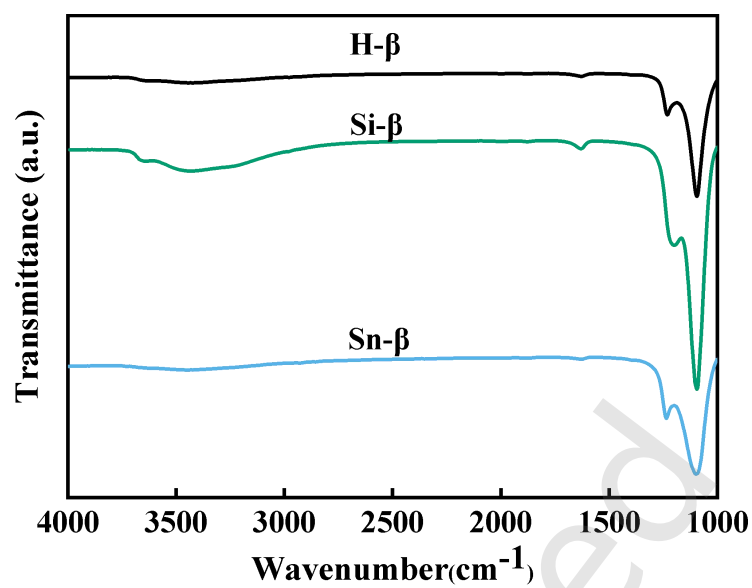


Fig. S3. FT-IR spectra of H-β, Si-β, and Sn-β.

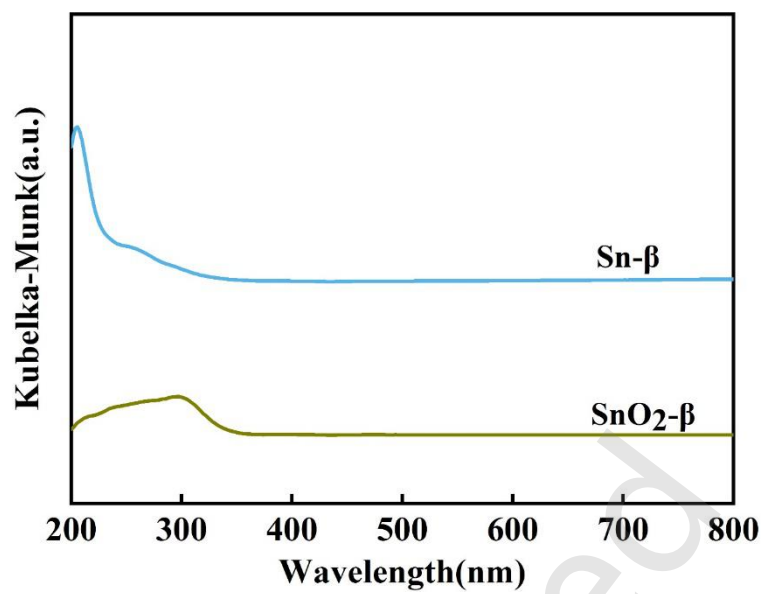


Fig. S4. UV-vis spectra of Sn-β and SnO₂-β.

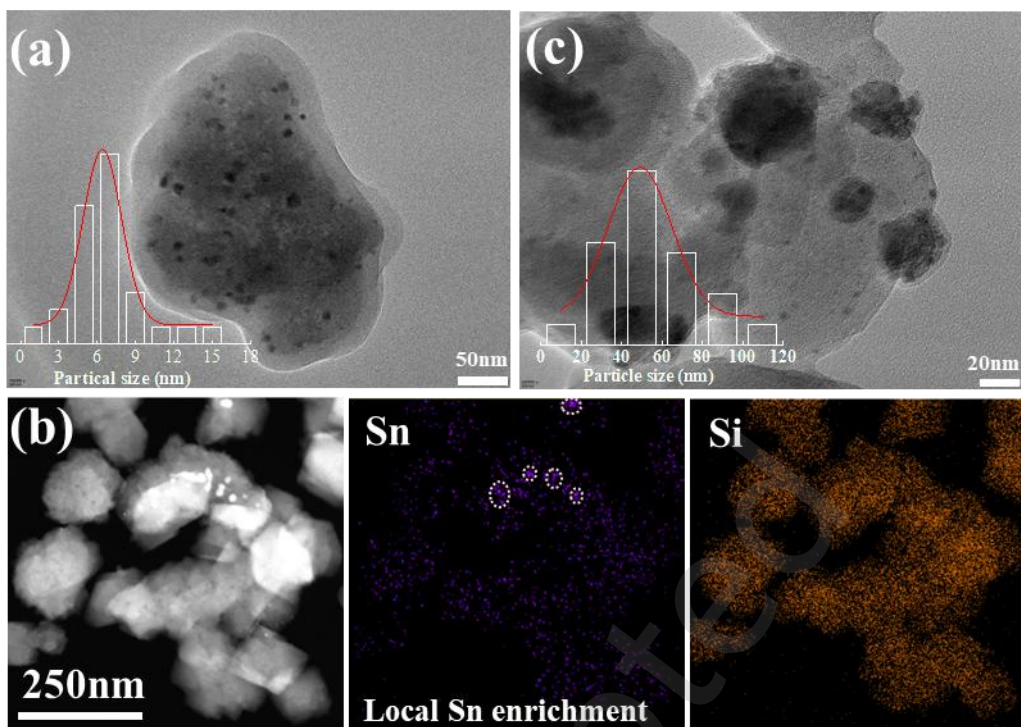


Fig. S5. TEM images of reduced Pt/Sn- β at 250 °C (a), 540 °C (b) and 650 °C (c).

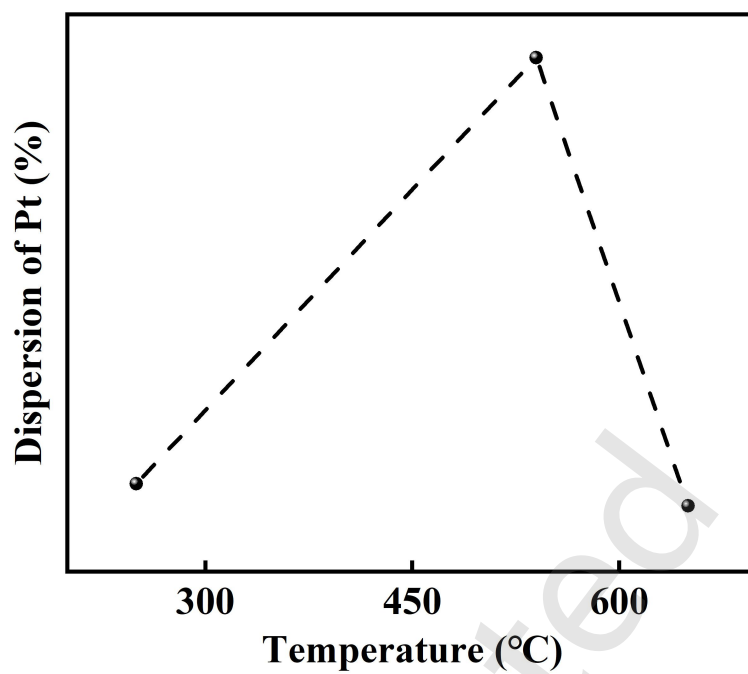


Fig. S6. Pt dispersion of Pt/Sn-β as a function of reduction temperature.

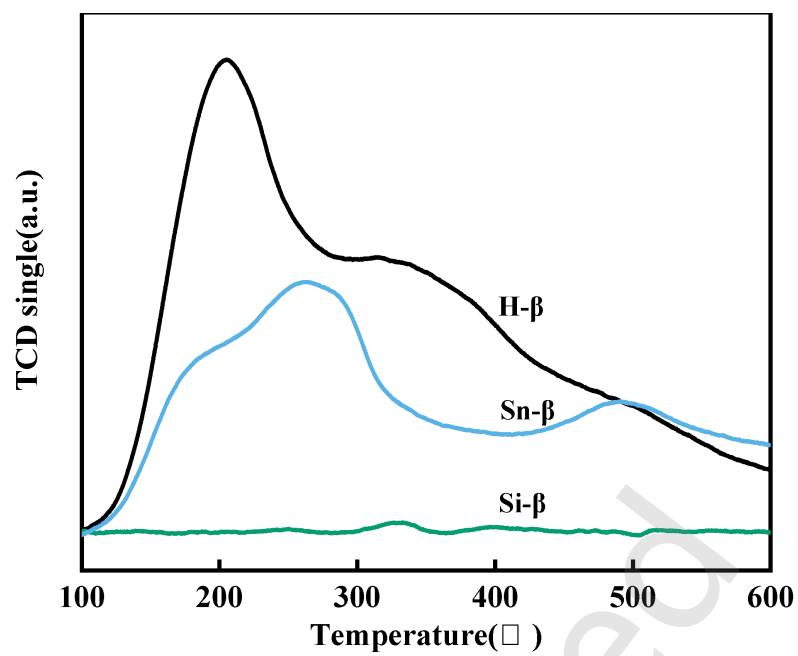


Fig. S7. NH₃-TPD profiles of supports.

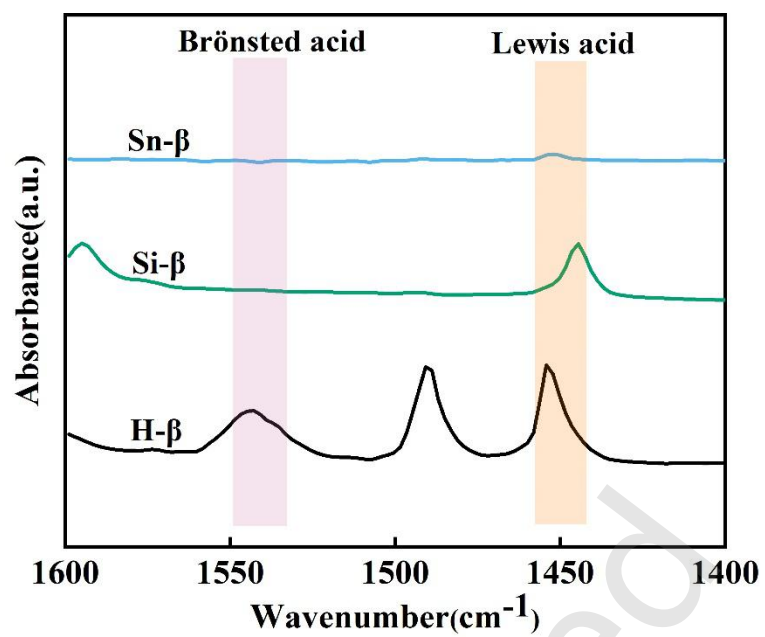


Fig. S8. Py-IR spectra of H-β, Si-β, and Sn-β.

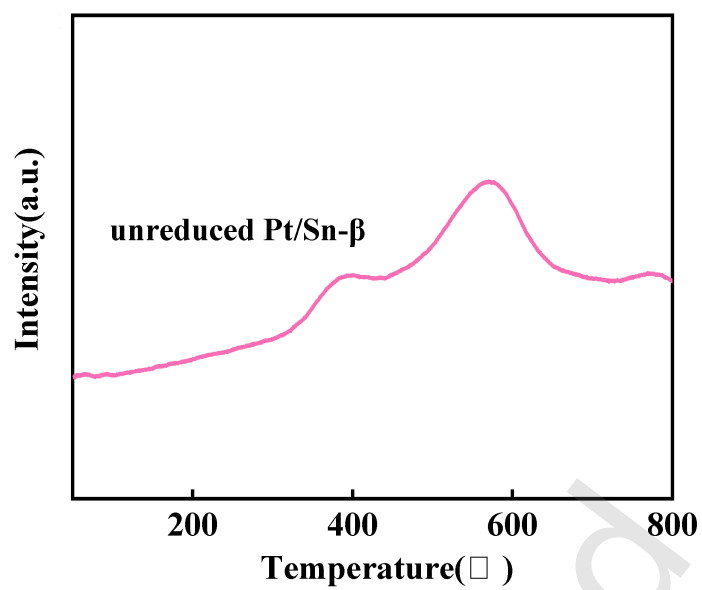


Fig. S9. H₂-TPR profile of the unreduced Pt/Sn-β catalyst.

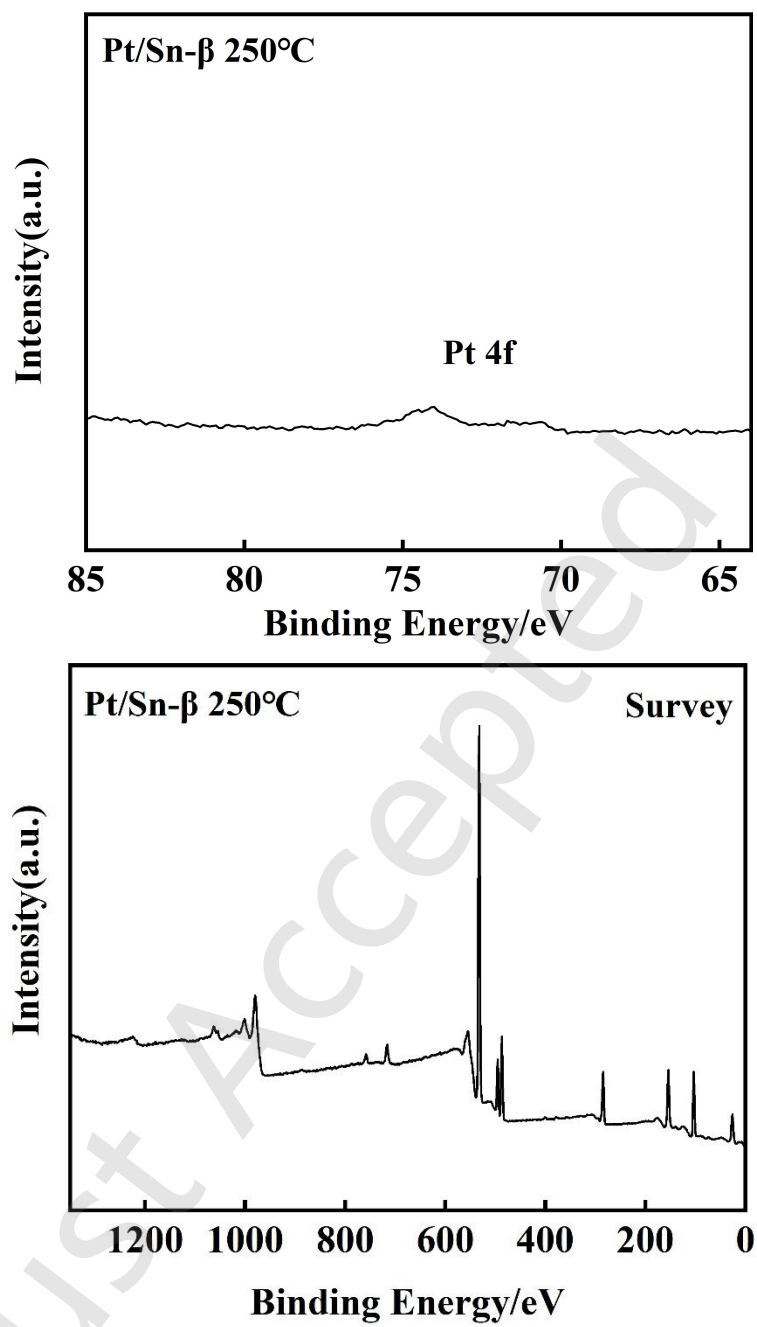


Fig. S10. XPS Pt 4f and survey spectra of catalysts reduced at 250 °C.

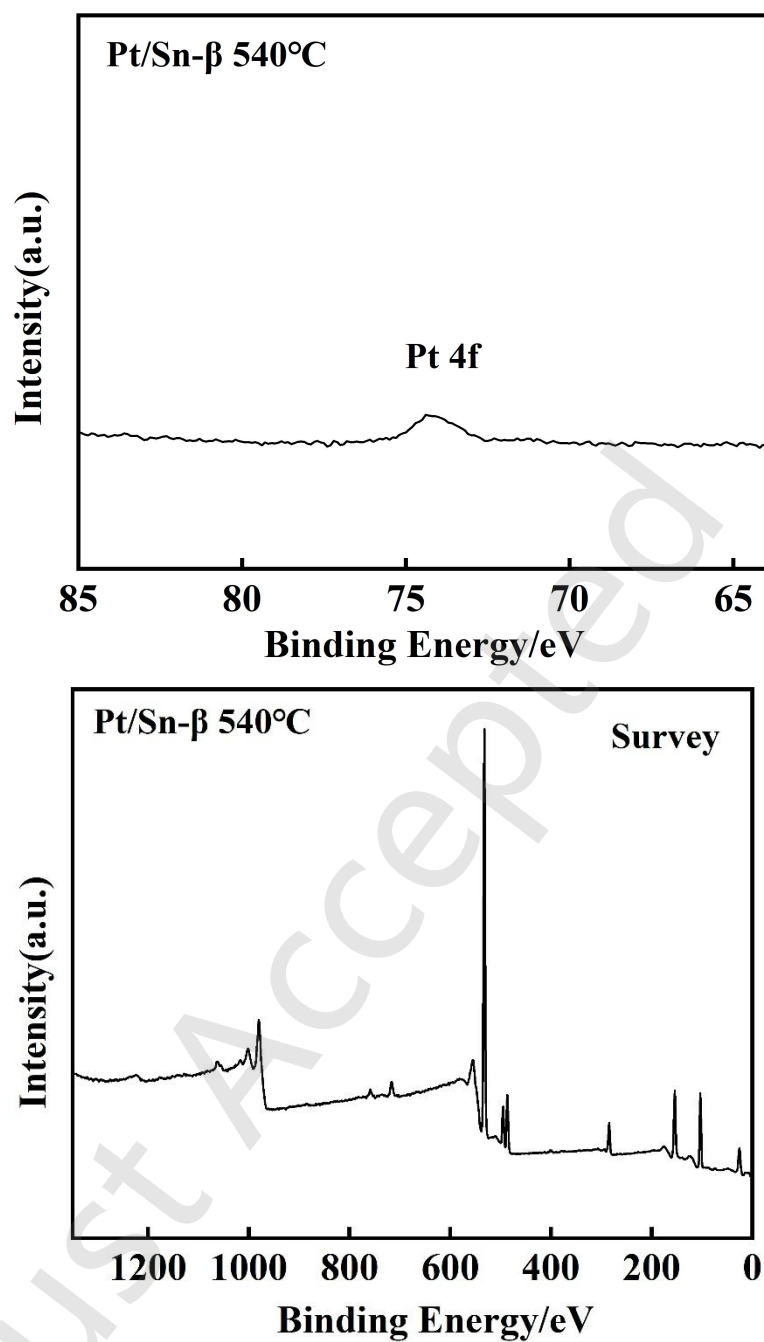


Fig. S11. XPS Pt 4f and survey spectra of catalysts reduced at 540 °C.

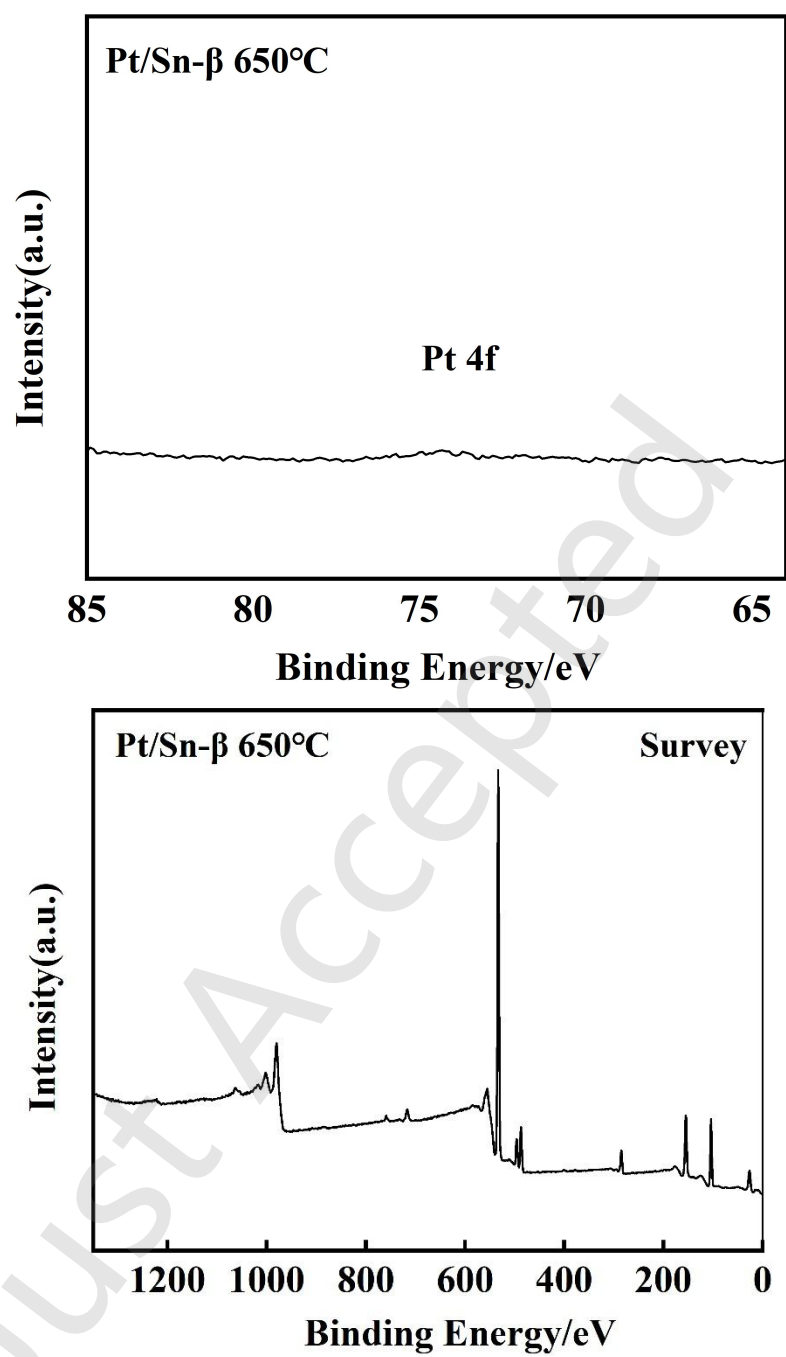


Fig. S12. XPS Pt 4f and survey spectra of catalysts reduced at 650 °C.

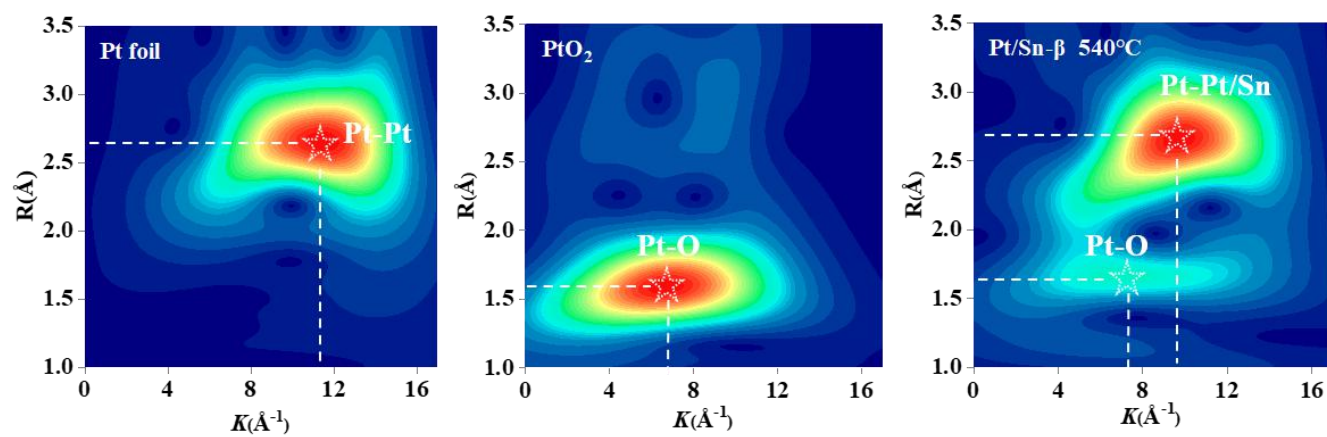


Fig. S13. Pt L_3 -edge wavelet-transformed EXAFS signals of (a) Pt foil, (b) PtO_2 , and (c) Pt/Sn- β 540 °C.

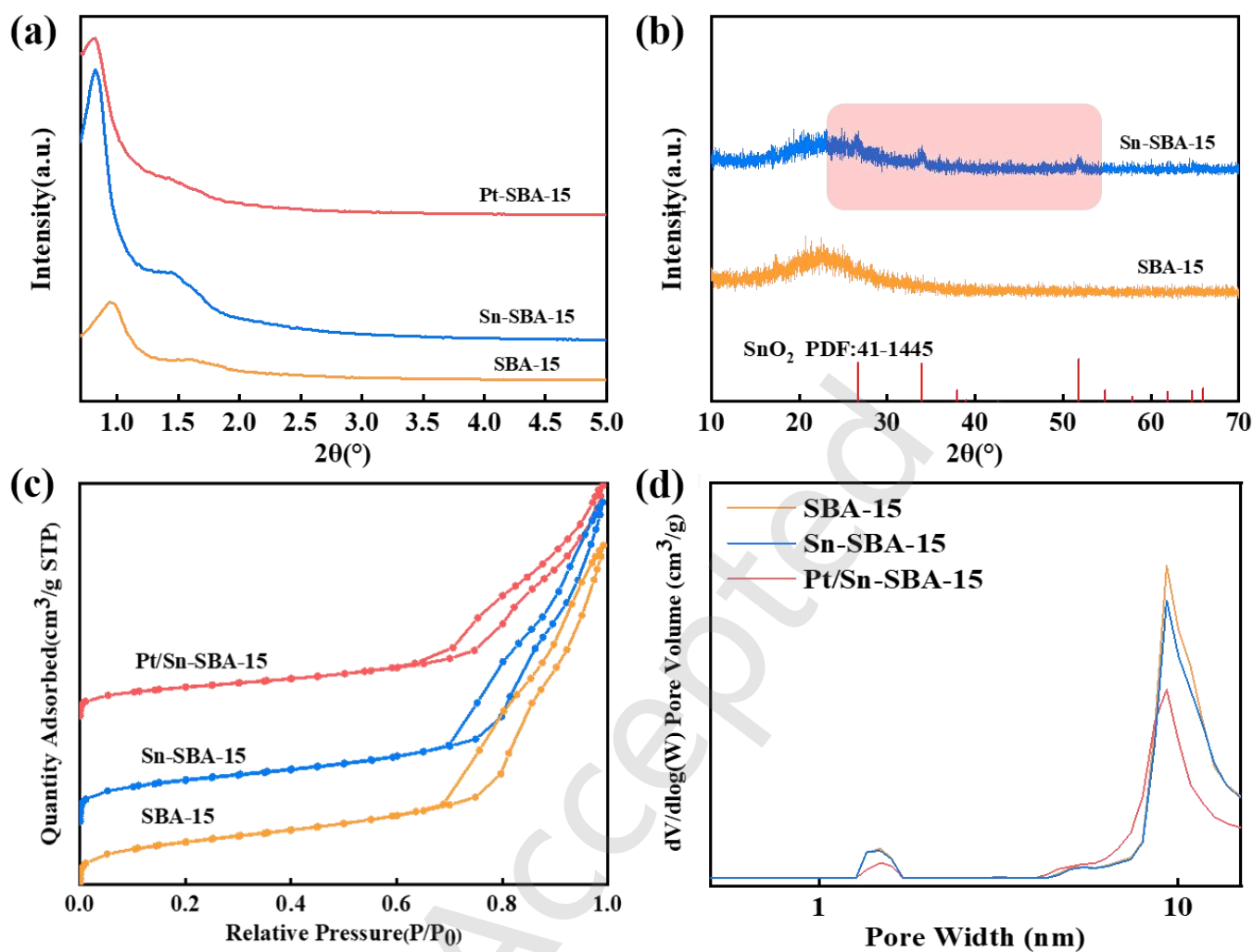


Fig. S14. Low-angle X-ray diffraction patterns (a), wide-angle X-ray diffraction patterns (b), N_2 adsorption-desorption isotherms (c), and pore-size distributions (d) of SBA-15, Sn-SBA-15, and Pt/Sn-SBA-15.

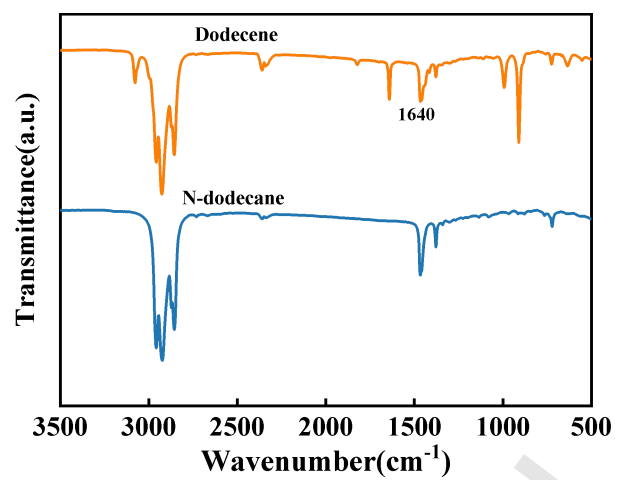


Fig. S15. FT-IR spectra of n-dodecane and dodecene.

Reference:

- [1] He, S.; Wang, B.; Dai, X.; Sun, C.; Bai, Z.; Wang, X.; Guo, Q. Industrial development of long chain paraffin (n-C₁₀–C₁₃) dehydrogenation catalysts and the deactivation characterization. *Chem. Eng. J.* **2015**, 275, 298-304.
- [2] Lu, Z.; Ji, S.; Liu, H.; Li, C. Preparation and Characterization of Pt-Sn/SBA-15 Catalysts and Their Catalytic Performances for Long Chain Alkane Dehydrogenation. *Chinese Journal of Chemical Engineering*, **2008**, 16(5): 740-745.
- [3] Meng, X.; Duan, L.; Zhang, L.; Zhang, D.; Yang, P.; Qin, H.; Zhang, Y.; Xiao, Sh.; Duan, L.; Zhou, R. Long-Chain Alkane Dehydrogenation over Hierarchically Porous Ti-Doped Pt–Sn–K/TiO₂–Al₂O₃ Catalysts. *Kinet. Catal.* **2022**, 62, S30-S37.
- [4] Cui, M.-T.; Wang, Z.; Li, X.-B.; Li, M.-S. Synthesis of ZSM-5 containing framework iron and catalytic performance of supported Pt catalysts in dehydrogenation of n-dodecane. *Chinese Journal of Inorganic Chemistry* **2020**, 36, 885-892.
- [5] Yu, P.; Cui, M.-T.; Li, Q.; Wang, D.; Wang, Z.; Li, M.-S.; Li, X.-B. Active, selective and stable Pt/Fe-silicalite-1 catalyst for dehydrogenation of n-dodecane to linear mono-dodecene. *Applied Catalysis A: General* **2020**, 608, 117860.