

Highly Efficient Catalytic Propane Dehydrogenation Driven by MFI Zeolite Defect Sites

Corresponding Author: Professor Jorge Gascon

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors report a Pt confined in Sn-MFI zeolite with abundant framework defects, obtained by one-pot hydrothermal synthesis. The Pt@Sn-MFI catalyst showed high propane conversion, propene selectivity and stability in the propane dehydrogenation reaction with diluted propane feed. However, in industry, pure propane feed is used. The authors are strongly suggested to evaluate the catalytic performance of Pt@Sn-MFI under the reaction condition closer to industrial standard. Additionally, the Si-OH groups are supposed to favor the propane dehydrogenation reaction and a reaction pathway assisted by Si-OH in the framework was proposed for the propane dehydrogenation. The authors did not provide an accurate structure model to explain the distribution of Pt, Sn, and Si-OH groups in MFI structure. Moreover, the proofs for the role of Si-OH were not solid enough and the structural model for theoretical calculations is not suitable without considering the MFI structure. Thus, this paper is not suitable for Nature Communications.

Here are some detail issues:

(1) In the Fig. 2a, the Si-OH should exist in hydroxyl nests, as indicated by the band around 3500 cm⁻¹. However, only single Si-OH group was given in the structural model in Fig. 5e. The structural model in Fig. 5e is wrong or far from accurate. Then, the theoretical calculations based on this structural model is also unconvincing. Moreover, the authors used the amorphous SiO₂ to replace the crystalline MFI structure with pores. It is not appropriate here because the confinement environment is totally different between SiO₂ and MFI structure.

(2) The signal in EXAFS spectroscopy at 1.6 Å does not necessarily indicates the interactions between the defect and Pt sites. The Pt-O-Sn interaction can also contribute to this signal (Page 7, line 202-205). Why did not the authors consider the interaction between Pt and Sn? Moreover, is the coordination number of Pt-O (0.5) reasonable (Page 8, line 235-240)? The authors are strongly suggested to provide the accurate description of the interaction between Pt and Sn as well as defective sites in MFI structure.

(3) "There is no doubt that the H atoms in the HD originate from propane, indicating that the Si-OD promotes the C-H cleave of propane to form and release the HD." There is no inherent relationship between these two statements; the author should provide more direct evidence.

(4) What is the regeneration performance of the catalysts? I believe that the reusability of the catalyst is more important than long-term one-way stability.

(5) The substrates in the propane dehydrogenation reaction are relatively small molecules. The mass transfer difference should not be the reason (Page 9-10, line 279-280).

(6) Why did the authors use two kinds of TPAOH solution with different concentrations during the synthesis of MFI related catalysts? The authors are suggested to discuss the reason why the introduction of Sn source into the synthesis of MFI zeolite helped to create more defective sites or mesopores and cite some references. How was the defect-free Pt@Sn-MFI synthesized?

(7) Since there are numerous Si-OH groups in MFI structure, the contribution of silanol groups to this band at 957 cm⁻¹ in Fig. 2c must be eliminated, by a pretreatment under vacuum at elevated temperature.

(8) Please provide the XRD pattern of the sample with Sn/Pt ratio of 6, because too much Sn may hinder the crystallization of MFI structure (Page 9, line 263-266). The authors should provide proofs for the existence of extra-framework Sn (Page 9, line 270-271).

(9) SEM images can not provide the proofs for the existence of mesopores (Page 5, line 145-146). Pt was not proved to be confined inside the pore channels of MFI structure (Page 6, line 148-149). The TEM technique provides only a projection of a specific crystal plane and cannot conclusively prove that these Pt species are located within the MFI structure. (Page 7, line 188-190)

- (10) Why did the EDTA-Sn complex enhance the NMR selectivity? What is the meaning of selectivity here? (Page 6, line 165-166)
- (11) How did the authors calculate the propene yield? It is supposed to be 59%? (Page 9, line 259)
- (12) The difference among the three samples in Supplementary Fig. 11 can be ignored. The authors may monitor the C₃H₆-desorption experiment through in-situ DRIFTS.
- (13) The authors should indicate the meaning of color and the arrows in Fig. 5a and c.
- (14) The authors should provide more detail information for the in-situ DRIFTS with CD₃CN as the probe molecules, including the temperature and duration of the adsorption and desorption process.
- (15) The complete of TPAOH under H₂/N₂ flow should be confirmed by TG analysis.
- (16) The intensities of the CO adsorbed IR spectra in Figure 3d should be provided.

Reviewer #2

(Remarks to the Author)

In the manuscript titled "Highly Efficient Catalytic Propane Dehydrogenation Driven by MFI Zeolite Defect Sites," the researchers synthesized a pure siliceous zeolite MFI-supported Pt-Sn catalyst using a modified ligand-protected one-pot hydrothermal method. This catalyst demonstrated a propylene selectivity of over 98.5% at a gas hourly space velocity of 9600 mL gcat⁻¹ h⁻¹ and 550 °C, maintaining stability for at least 120 hours. Additionally, the authors employed various characterization techniques, isotope-labeled experiments, and DFT calculations to identify the active sites on the catalyst and elucidate the reaction mechanism of propane dehydrogenation (PDH). The direction taken by the authors is intriguing, and the development of efficient catalysts for propane dehydrogenation is undoubtedly significant for the chemical industry.

However, the reviewer has expressed concerns regarding the characterization of the catalysts. Before further consideration, the authors should address these concerns as outlined below:

1. The authors identified the [SiO]₃-Sn-O-Ptn as the active sites for the Pt@Sn-MFI catalyst, citing reference 23 for support (J. Catal. 397, 44-57 (2021)). Do the authors have additional references that could support this chemical structure? What are the differences between the catalyst described in this manuscript and the one in reference 23? In other words, what accounts for the superior PDH performance of the catalyst developed in this work compared to previous investigations, such as reference 23?
2. The authors employed ex-situ X-ray absorption spectroscopy (XAS) to determine the structural details of Pt. However, Pt species have the potential to oxidize in air (ACS Catal. 9, 10626-10639 (2019)), making in-situ XAS experiments more reliable (Nat. Catal. 4, 453-456 (2021)). Additionally, conducting in-situ experiments for Sn K-edge XANES and Sn K-edge EXAFS spectra would also help identify the chemical structure of the Sn element (ACS Catal. 14, 2859-2871 (2024)).
3. The captions for Supplementary Fig. 10 c and d are missing.
4. The authors compared the PDH performance of Pt@Sn-MFI (Con. 59.2% & Sel. 98.5%) with that of PtSn/MFI (Con. 58.3% & Sel. 98.2%) synthesized using the traditional impregnation method. However, the performance of Pt@Sn-MFI does not appear to be significantly better. The authors should provide a more detailed discussion on the differences between the Pt@Sn-MFI catalysts and the traditional PtSn/MFI catalysts.
5. One highlight of the Pt@Sn-MFI catalyst is its extremely high stability in PDH while maintaining a high selectivity for propylene and conversion. However, the authors did not provide sufficient experimental results to support the reasons behind this catalyst's enhanced PDH stability. What is the relationship between the chemical structure of Pt@Sn-MFI and its high stability?
6. Comparing the activities of the Pt@Sn-MFI catalysts with those of Pt and PtSn catalysts reported in the literature is challenging due to variations in temperature, propane partial pressure, hydrogen partial pressure, propane conversion, and the approach to equilibrium in each study. It would be more appropriate to compare the performance based on the apparent forward rate coefficient for PDH, as suggested in references such as ACS Catal. 14, 3986-4000 (2024).

Reviewer #3

(Remarks to the Author)

The manuscript designed a robust Pt@Sn-MFI catalyst for efficient propane dehydrogenation (PDH) to propylene by engineering defect sites within the MFI zeolite framework. This work proposes a novel hydroxyl-assisted PDH reaction mechanism, underpinned by extensive experimental characterization and density functional theory (DFT) calculations. The findings highlight the synergistic role of Pt sites within the defect-rich Sn-MFI structure, facilitating selective C-H activation and stability. Overall, the manuscript is well-structured and methodologically rigorous. However, minor revisions are recommended before publication in Nature Communications. The detailed suggestions are listed below:

1. The abstract contains detailed information that could be condensed to more directly emphasize the most impactful findings.
2. It is generally understood that PtSn alloy is often considered the active site for catalyzing PDH. Could the authors clarify why Sn does not form an alloy with Pt in the Pt@Sn-MFI catalyst, particularly given the proximity of Pt and Sn?
3. Please explain the advantages of the active site structure ([SiO]₃-Sn-O-Ptn) in Pt@Sn-MFI compared to conventional PtSn alloys, especially in terms of catalytic performance.
4. In the figure legends for Figures 1 and 2, the specific modes used for the UV-Vis and IR spectra, respectively, are unclear. Clear labeling of these modes is suggested.
5. It appears that phase correction has not been applied in Figures 3e and 3f. So, using R+α as the x-axis may not be

accurate. Please re-evaluate the fitting process for these data to ensure accurate representation.

6. In Figures 4a–c, the performance data for different catalysts had been collected at different time points rather than at the same time points. Could the authors clarify the reason for this timing discrepancy?

7. The font clarity in Figures 5a and 5c should be improved for better readability.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed most of the issues in the revised manuscript; however, there are still problems regarding the construction of the theoretical calculation model, particularly concerning the catalytic centers. On one hand, the number of Sn atoms in a single MFI unit cell should consider the framework Si/Sn ratio. On the other hand, the number of Pt metal atoms in the catalytic center should take into account the results from TEM and EXAFS. Clearly, a catalytic center composed of three Pt metal atoms does not match either of these results. TEM shows that the particle size of the catalytic center is approximately 1.1 nm, which should be larger than the size of three Pt metal atoms. Additionally, the Pt-Pt coordination number (CN) is 6.7, inconsistent with the assumption of three atoms.

Given these discrepancies, can this structural model truly reflect the catalytic reaction mechanism? Since one of the most important evidence for the hydroxy-assisted reaction in this study is derived from theoretical calculations, if the structural model itself is incorrect, can the results still be considered reliable?

Reviewer #2

(Remarks to the Author)

Although the authors addressed some of the comments, they were unable to conduct the in-situ XAS experiment due to "experimental constraints". This limitation compromises the quality and scientific contribution of the work.

Reviewer #3

(Remarks to the Author)

The authors have properly answered my question and I recommend its publication in "Nature Communication".

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors reconstructed a structural model in which 20 Pt atoms are anchored by 5 Sn atoms within an MFI framework containing mesopores. However, I still find this model highly questionable. Firstly, considering that the Sn content per unit cell is only 0.5, how is it possible to locally enrich 5 Sn atoms in such a confined region? What kind of synthesis method could realistically achieve such a high local concentration of Sn? Secondly, the EXAFS data shows an average Pt–Pt coordination number (CN) of 6.7, yet the maximum CN in the authors' 20-atom Pt cluster model is ~ 6. What's the average Pt–Pt coordination number for the 20-atom Pt cluster? Additionally, is the average Pt–O CN in this model consistent with EXAFS data? Furthermore, the 20-atom Pt model was not constructed based on experimental evidence but rather adapted from literature and then fitted to match the experimental results. This approach is fundamentally flawed.

Reviewer #2

(Remarks to the Author)

This reviewer has no further comments.

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Point-by-Point Responses to the Reviewers' Comments

Reviewer #1 (Remarks to the Author):

Comments 1: *The authors report a Pt confined in Sn-MFI zeolite with abundant framework defects, obtained by one-pot hydrothermal synthesis. The Pt@Sn-MFI catalyst showed high propane conversion, propene selectivity and stability in the propane dehydrogenation reaction with diluted propane feed. However, in industry, pure propane feed is used. The authors are strongly suggested to evaluate the catalytic performance of Pt@Sn-MFI under the reaction condition closer to industrial standard. Additionally, the Si-OH groups are supposed to favor the propane dehydrogenation reaction and a reaction pathway assisted by Si-OH in the framework was proposed for the propane dehydrogenation. The authors did not provide an accurate structure model to explain the distribution of Pt, Sn, and Si-OH groups in MFI structure. Moreover, the proofs for the role of Si-OH were not solid enough and the structural model for theoretical calculations is not suitable without considering the MFI structure. Thus, this paper is not suitable for Nature Communications.*

Response: We appreciate the reviewer for the insightful comments. We have carefully addressed the concerns raised by following point-by-point clarifications and conducting additional experiments to strengthen our findings.

Following the reviewers' comments, we carried out the dehydrogenation experiment of pure propane under near-industrial reaction conditions of $T = 550\text{ }^{\circ}\text{C}$, pure C_3H_8 , GHSV = $9600\text{ mL g}_{\text{cat}}^{-1}\text{h}^{-1}$. As shown in Figure R1, the Pt@Sn-MFI catalyst did not show significant signs of deactivation for 80 h of continuous operation. And the HAADF-STEM image and corresponding Pt cluster size dispersion of the spent Pt@Sn-MFI catalyst after the dehydrogenation experiment of pure propane show no obvious aggregation of the Pt nanoclusters, demonstrating their robust structure and excellent anti-sintering properties.

We appreciate the reviewer's concerns regarding the structural model and the proposed reaction pathway. In response, we have revised our catalyst model by replacing the amorphous SiO_2 with the crystalline MFI framework, incorporating Sn atoms into MFI structure and interacting with Pt clusters, which are located near Si-OH groups, guided by the principle of lowest energy, as well as including hydroxyl nests to more accurately reflect the actual catalyst structure (See revised model in Figure R3). This updated

model provides a more precise basis for theoretical analysis of the catalytic mechanism. Utilizing this updated model, we re-conducted DFT calculations to investigate the potential reaction pathway. Our studies focused on the adsorption of methyl (or methylene) groups onto Pt sites, as well as the subsequent formation and release of H₂ involving the dehydrogenation of propane, including the combination of hydrogen atoms from the methyl and methylene groups in propane, as well as the combination of hydrogen atoms from the methyl or methylene groups with hydrogen atoms from neighboring hydroxyl groups on the zeolite material. As illustrated in Figure R4, in the case of methyl adsorption on Pt sites, the energy relative to the initial state decreased to -0.580 eV. During the subsequent formation and release of H₂, it was evident that the energy required for the combination of H from the methyl group in propane with H from neighboring hydroxyl groups (-1.211 eV) was significantly lower than the energy required for the combination of H from the methyl group and H from the methylene group in propane (-0.177 eV). Similar phenomenon was observed for the adsorption of methylene groups on Pt sites, where the energy required for the combination of H from the methylene group in propane with H from neighboring hydroxyl groups (-0.692 eV) was much lower than the energy required for the combination of H from the methyl group and H from the methylene group in propane (-0.612 eV). These results strongly emphasize the crucial role of neighboring hydroxyl groups in the propane dehydrogenation process. Moreover, after the desorption of propylene from the Pt sites (-1.020 eV for methyl_hydroxy vs. -0.340 eV for methylene_hydroxy), the H in the remaining Pt-*H species readily spillovers (0.207 eV for methyl_hydroxy vs. 0.224 eV for methylene_hydroxy) to the previously unsaturated oxygen species, regenerating Si-OH.

In addition, following the reviewers' comments, we also considered the participation of hydroxyl nests in the propane dehydrogenation process, but the energy required for its hydrogen formation pathway involving hydroxyl nests is always much greater (> ~2 eV) than the energy required for hydrogen formation by the dehydrogenation pathways of methyl and methylene in propane alone (Figure R5). Furthermore, our previous *in-situ* DRIFTS data did not detect evidence supporting the involvement of hydroxyl nests in the dehydrogenation process (Supplementary Fig. 15), indicating that hydroxyl nests are unlikely to directly participate in propane dehydrogenation.

To provide more conclusive evidence for the participation of Si-OH groups in the

propane dehydrogenation reaction, we conducted [a new mass spectrometry experiment by using isotopically labeled propane \(\$C_3D_8\$ \)](#) as the feed gas to trace the dehydrogenation process. The results, shown in Figure R6, demonstrate the presence of both D_2 and HD signals upon introducing C_3D_8 . The gradual decrease in the HD signal as the reaction proceeds, coupled with the rapid decrease of both D_2 and HD signals when the C_3D_8 bypasses the catalyst, strongly supports the involvement of Si-OH groups in the dehydrogenation process. These findings are consistent with the original submission and offer solid experimental proof for the role of Si-OH groups in the catalytic reaction. Therefore, **we respectfully retain the hydroxyl-assisted propane dehydrogenation route rather than the hydroxy-nest-assisted route, as it remains consistent with the experimental observations.**

We have added these discussions in the revised manuscript and placed the new results in Figure 5 and Supplementary Figs. 9, 10, 19a and 21.

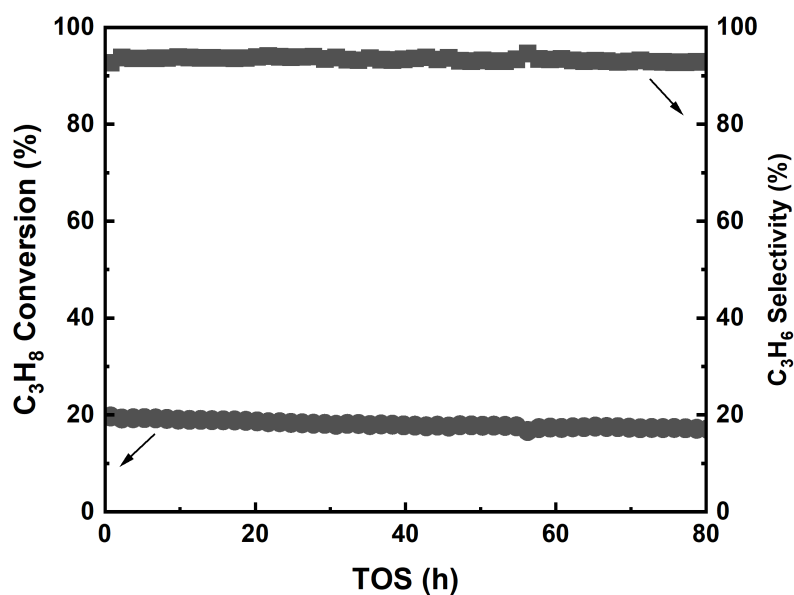


Figure R1. Stability evaluation of the Pt@Sn-MFI catalyst for the dehydrogenation of pure propane. Reaction conditions: $T = 550^\circ C$, pure C_3H_8 , GHSV = $9600 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$.

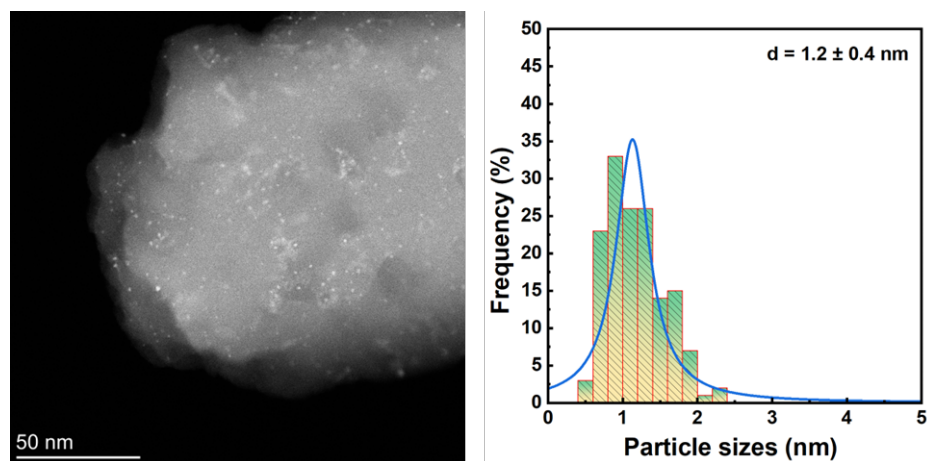


Figure R2. Pt dispersion of spent Pt@Sn-MFI catalyst under pure propane flow.
a, HAADF-STEM image. **b**, Corresponding Pt cluster size distribution.

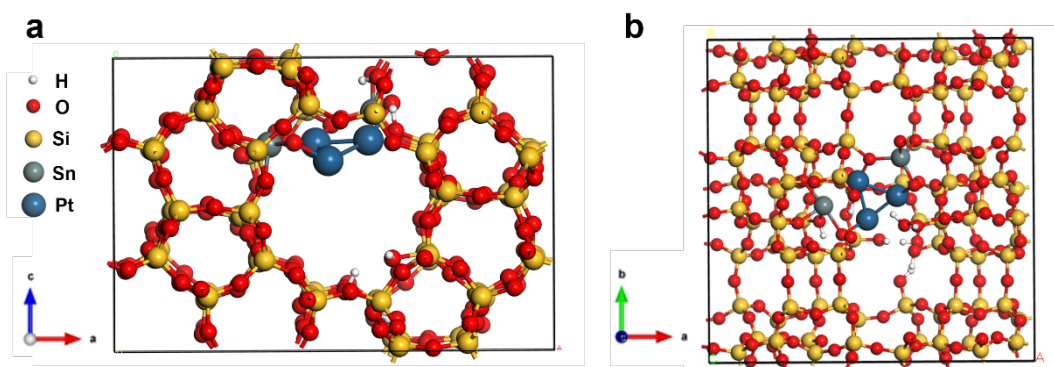


Figure R3. Stable structure of Sn doped into MFI framework bonding with Pt. **a**, View from the x-axis. **b**, View from the z-axis.

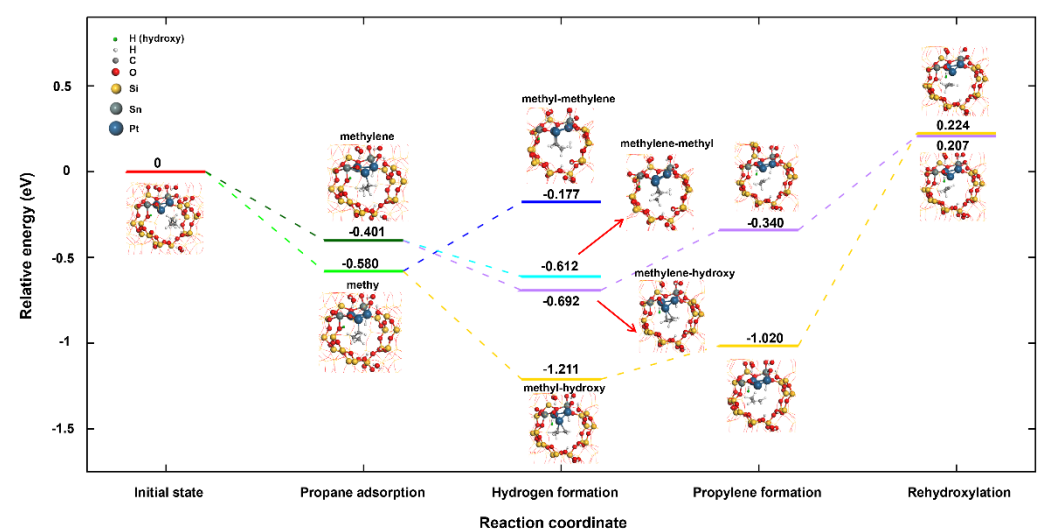


Figure R4. Reaction pathway of propane dehydrogenation. The values above the

solid line represent the energy relative to the initial state (defined as zero). Specifically, in the initial state, free propane was confined within MFI channel. In the propane adsorption stage, the adsorption of the methyl (or methylene) group in propane on Pt sites was considered. In the hydrogen formation and desorption stage, hydrogen from propane's methyl and methylene groups, as well as from their combination (either methyl or methylene) with adjacent hydroxyl groups, was considered. In the propylene formation stage, the analysis focuses on two pathways (i.e., the methyl_hydroxyl and methylene_hydroxyl) that are considered more likely to occur in the reaction. In the rehydroxylation stage, H originating from propane on Pt sites spillovers to adjacent unsaturated oxygen species, resulting in the regeneration of hydroxyl groups. The green, white, grey, red, yellow, dimgrey and darkblue spheres represent H in hydroxyl, H in propane, C, O, Si, Sn, and Pt, respectively.

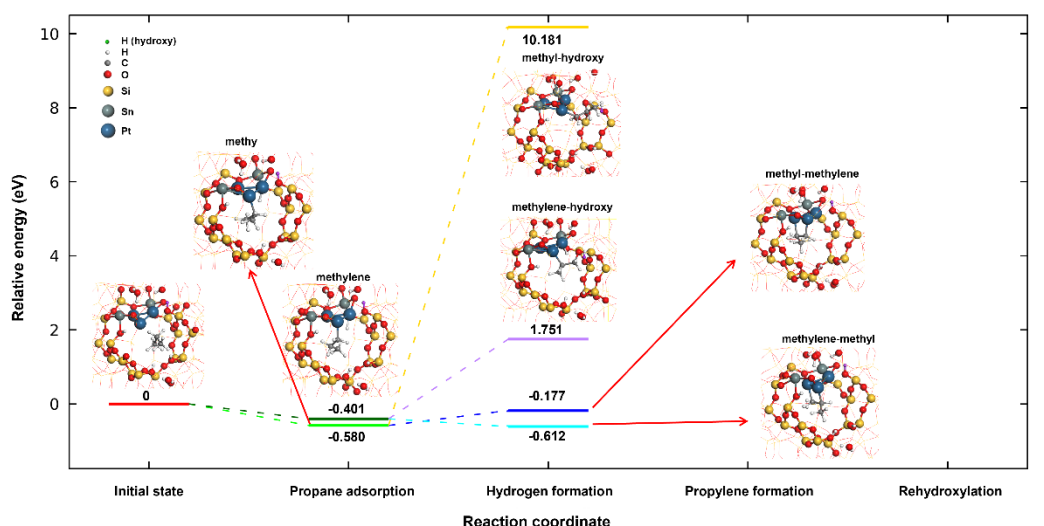


Figure R5. Reaction pathway for propane dehydrogenation involving hydroxyl nests. The values above the solid line represent the energy relative to the initial state (defined as zero). Specifically, in the initial state, free propane was confined within MFI channel. In the propane adsorption stage, the adsorption of the methyl (or methylene) group in propane on Pt sites was considered. In the hydrogen formation and desorption stage, hydrogen from propane's methyl and methylene groups, as well as from their combination (either methyl or methylene) with adjacent hydroxyl groups, was considered. The green, white, grey, red, yellow, dimgrey and darkblue spheres represent

H in hydroxyl, H in propane, C, O, Si, Sn, and Pt, respectively.

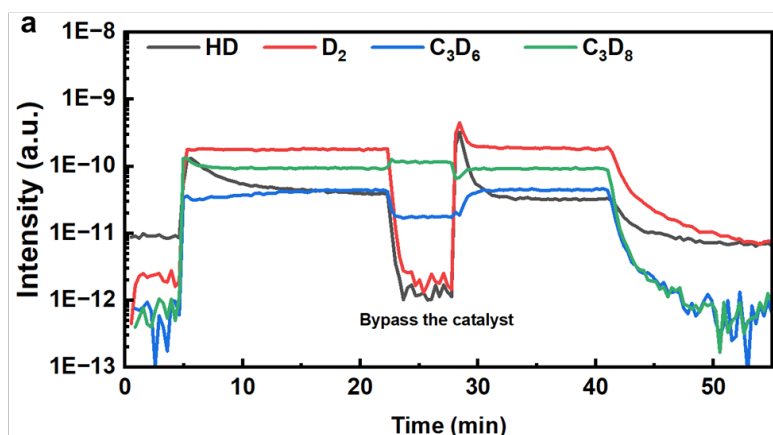


Figure R6. Mass spectra tracing the dehydrogenation process of C_3D_8 over $Pt@Sn-MFI$.

The related change is described in the revised manuscript as below.

Additionally, the stability of the $Pt@Sn-MFI$ catalyst was assessed under near-industrial reaction conditions (i.e., $T = 550\text{ }^{\circ}C$, pure C_3H_8 , $GHSV = 9600\text{ mL g}_{cat}^{-1}h^{-1}$), as well. As shown in Supplementary Fig. 9, the $Pt@Sn-MFI$ catalyst exhibited no significant signs of deactivation over 80 h of continuous operation. The HAADF-STEM image and corresponding Pt cluster size dispersion of the spent $Pt@Sn-MFI$ catalyst following the pure propane dehydrogenation experiment showed no obvious aggregation of the Pt nanoclusters (Supplementary Fig. 10), demonstrating their robust structure and excellent anti-sintering properties.

Based on the structural characteristics of the $Pt@Sn-MFI$ catalyst discussed above, a stable Sn-doped MFI system rich in hydroxyl groups was created by substituting Si atoms with Sn atoms, followed by bonding Pt to Sn via Sn-O-Pt bonds to achieve a stable structure of Sn-doped MFI with bonded Pt, guided by the principle of lowest energy (Supplementary Fig. 21).

To further trace the dehydrogenation process, MS experiments were performed using isotopically labeled propane (C_3D_8) as the feed gas. As shown in Supplementary Fig. 19a, both D_2 and HD signals were detected upon introducing C_3D_8 . The gradual decrease in HD signal over time, along with the rapid disappearance of both D_2 and HD signals when C_3D_8 bypassed the catalyst, strongly supports the involvement of Si–

OH groups in the dehydrogenation process.

The 288-atom MFI zeolite structure was used as the basis for our calculations. The geometric parameters of the model were determined as follows: $a=20.108\text{ \AA}$, $b=19.918\text{ \AA}$, $c=13.392\text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$. All the calculations were performed under the framework of density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP).^{57,58} The electronic exchange-correlation interactions were described using the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA).⁵⁹ In the calculations, the energy cut-off of the plane-wave basis was set to 520 eV. For ionic position relaxation, the Brillouin zone integration was carried out at Gamma point, and for the single point energy calculation, a $2\times 2\times 2$ Monkhorst-Pack K-grid was employed. The models were optimized using the conjugate gradient algorithm, with the maximum force of 0.05 eV/ $\text{\AA}$. The total energy was well converged to less than 1×10^{-5} eV.

To simulate the model of this catalyst, where Sn was first doped on the Si sites of 10-members ring surface, and then Pt was injected, connecting with Sn bridged by O atoms. Our methodology adhered to the principle of minimizing energy while adding Sn and Pt atoms one by one, until the model showed significant distortion. Moreover, Pt atoms were constrained to cluster together as soon as possible. Our calculation found that the number of Sn atoms should be limited to around two, and maintaining an appropriate distance between the Sn dopants was crucial. Similar considerations applied to Pt atoms. Ultimately, the stable structure of Sn-doped on the MFI zeolite structure with bonded Pt was obtained, where O atoms connected to Sn played a key role. Based on this stable structure ($\text{Si}_{92}\text{O}_{191}\text{H}_5\text{Sn}_2\text{Pt}_3$), we investigated four different reaction pathways.

Comments 2: Here are some detail issues:

In the Fig. 2a, the Si-OH should exist in hydroxyl nests, as indicated by the band around 3500 cm^{-1} . However, only single Si-OH group was given in the structural model in Fig. 5e. The structural model in Fig. 5e is wrong or far from accurate. Then, the theoretical

calculations based on this structural model is also unconvincing. Moreover, the authors used the amorphous SiO₂ to replace the crystalline MFI structure with pores. It is not appropriate here because the confinement environment is totally different between SiO₂ and MFI structure.

Response: We appreciate the reviewer's insightful comments regarding our structural model. In response, we have updated our catalyst model by replacing the amorphous SiO₂ with the crystalline MFI framework, incorporating hydroxyl nests to more accurately reflect the actual catalyst structure. Please see **Response to Comments R1** for detail.

Comments 3: *The signal in EXAFS spectroscopy at 1.6 Å does not necessarily indicates the interactions between the defect and Pt sites. The Pt-O-Sn interaction can also contribute to this signal (Page 7, line 202-205). Why did not the authors consider the interaction between Pt and Sn? Moreover, is the coordination number of Pt-O (0.5) reasonable (Page 8, line 235-240)? The authors are strongly suggested to provide the accurate description of the interaction between Pt and Sn as well as defective sites in MFI structure.*

Response: We appreciate this valuable suggestion. We totally agree with the reviewer's point of view that the Pt–O–Sn interaction contributes to the 1.6 Å signal in EXAFS, and we apologize for the previous misinterpretation. We have made the changes in the revised manuscript.

For the average coordination number of Pt–O, our EXAFS fitting models indicated that an average coordination number of 0.5 provided the best fit with satisfactory R-factor values. Given that the Pt clusters are estimated to have a size of around 1.1 nm, a significant portion of the Pt atoms in the clusters are coordinated with neighboring Pt atoms, rather than oxygen atoms, which explains the relatively low coordination number of Pt–O.

To provide a clearer and more precise explanation of the interactions between Pt, Sn, and the defective sites within the MFI structure, we have also revised the manuscript to include an atomic-level structural model for Pt@Sn-MFI. This model incorporates the

Pt structure anchored by integrated Sn species within MFI (i.e., $[\text{SiO}]_3\text{-Sn-O-Pt}_n$) and the abundant zeolite defects (i.e., Si-OH) in the proximity, which allows for a more accurate representation of the catalyst's structure and interactions. We believe these updates will better address the reviewer's concerns and improve the clarity of our structural analysis.

The related change is described in the revised manuscript as below.

...due to a robust Pt-O-Sn interaction in the Pt@Sn-MFI. These findings further suggest that the integrated Sn species primarily exist at structural defects, serving as anchoring sites for the ultrafine Pt clusters by forming $[\text{SiO}]_3\text{-Sn-O-Pt}_n$ complexes.

...we propose a probable atomic-level structure model for Pt@Sn-MFI, which combines the Pt structure ($[\text{SiO}]_3\text{-Sn-O-Pt}_n$) with abundant zeolite defects (i.e., Si-OH) in the proximity, as shown in Fig. 3g.

Comments 4: *“There is no doubt that the H atoms in the HD originate from propane, indicating that the Si-OD promotes the C-H cleave of propane to form and release the HD.” There is no inherent relationship between these two statements; the author should provide more direct evidence.*

Response: We appreciate this valuable suggestion. Following the Reviewer's Comments, we performed additional mass spectrometry experiments by using isotopically labeled propane (C_3D_8) as the feed gas to trace the dehydrogenation process. As shown in Figure R7, compared with the hydroxyl-deficient Pt@Sn-MFI catalyst (Supplementary Figs. 20b-20c), the hydroxyl-enriched Pt@Sn-MFI catalyst exhibited stronger signals for C_3D_6 and HD during C_3D_8 feeding. This observation directly indicates that the Si-OH groups in the Pt@Sn-MFI catalyst facilitate the cleavage of C-D bonds of C_3D_8 and the formation of HD. We have added these additional results and discussions in the revised manuscript, with the new data provided in Supplementary Figure 19.

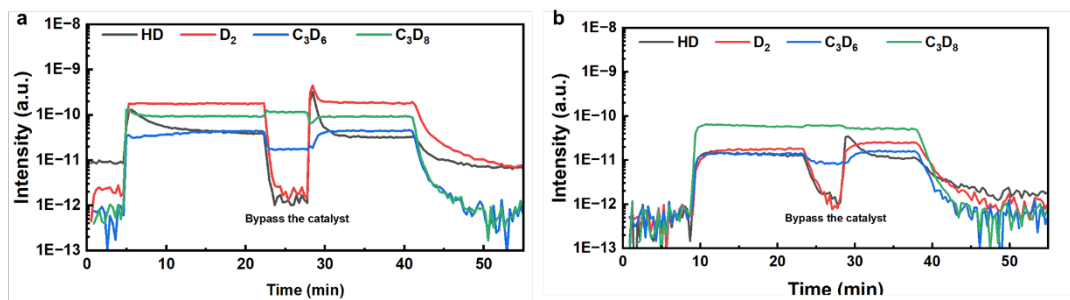


Figure R7. Mass spectra tracing the dehydrogenation of C_3D_8 . a, Pt@Sn-MFI. b, Defect-free Pt@Sn-MFI with negligible hydroxyl groups.

The related change is described in the revised manuscript as below.

To elucidate the advantage of Si-OH in the PDH reaction, we synthesized an additional defect-free Pt@Sn-MFI, characterized by an almost negligible presence of hydroxyl groups (Supplementary Figs. 20a-c). Compared with the defect-free Pt@Sn-MFI catalyst, the defect-enriched Pt@Sn-MFI catalyst exhibited stronger signals for C_3D_6 and HD during C_3D_8 feeding (Supplementary Fig. 19), indicating that the Si-OH in the Pt@Sn-MFI catalyst facilitates the cleavage of C-D bonds of C_3D_8 and the formation of HD. Furthermore, the defect-free Pt@Sn-MFI catalyst displayed lower C_3H_8 conversion (Supplementary Fig. 20d), further confirming the crucial role of zeolite defects in enhancing PDH activity.

Comments 5: *What is the regeneration performance of the catalysts? I believe that the reusability of the catalyst is more important than long-term one-way stability.*

Response: We appreciate the insightful comment regarding the importance of catalyst reusability. In response, we conducted regeneration experiments on spent Pt@Sn-MFI catalyst. The regeneration process involved treating the spent catalyst under a 20% O_2 / N_2 atmosphere at 500 °C for 0.5 h, followed by reduction under an H_2 flow at 550 °C. After three regeneration cycles, the catalyst retained approximately 89.9% of its initial propane conversion, while maintaining a high propylene selectivity of 99.7% (Figure R8). The HAADF-STEM image of spent Pt@Sn-MFI after three regeneration cycles showed that the majority of Pt species remained as clusters smaller than 2 nm in size (Figure R9), indicating minimal sintering and demonstrating the catalyst's robust

structural stability. These findings underscore the reusability of the Pt@Sn-MFI catalyst in propane dehydrogenation applications. We have added these additional results and discussions in the revised manuscript, with the new data provided in Supplementary Figs. 11 and 12.

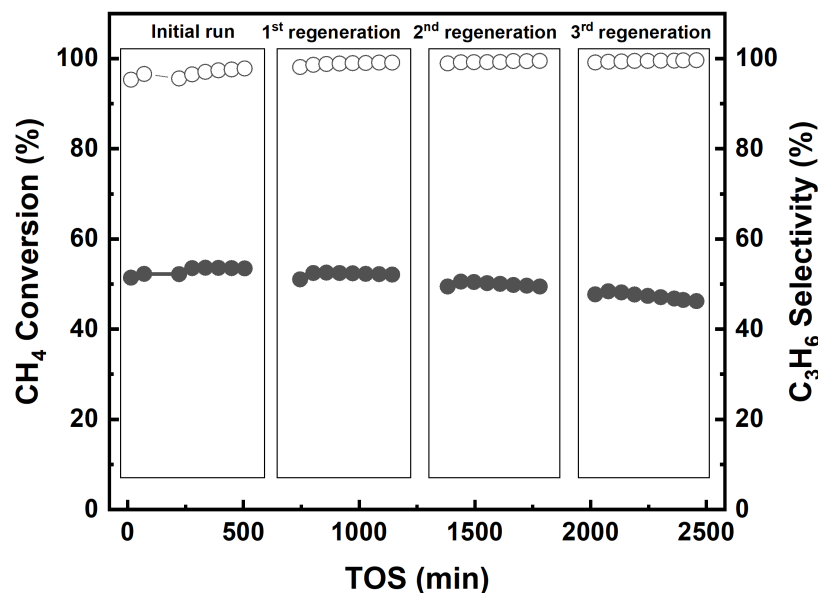


Figure R8. Dehydrogenation-oxidative regeneration test over the Pt@Sn-MFI catalyst. Reaction conditions were as follows: 1 bar, 550 °C, GHSV = 15000 mL g_{cat}⁻¹ h⁻¹. Regeneration conditions were as follows: 500 °C in air atmosphere for 30 min and subsequent 550 °C in H₂ for 1 h.

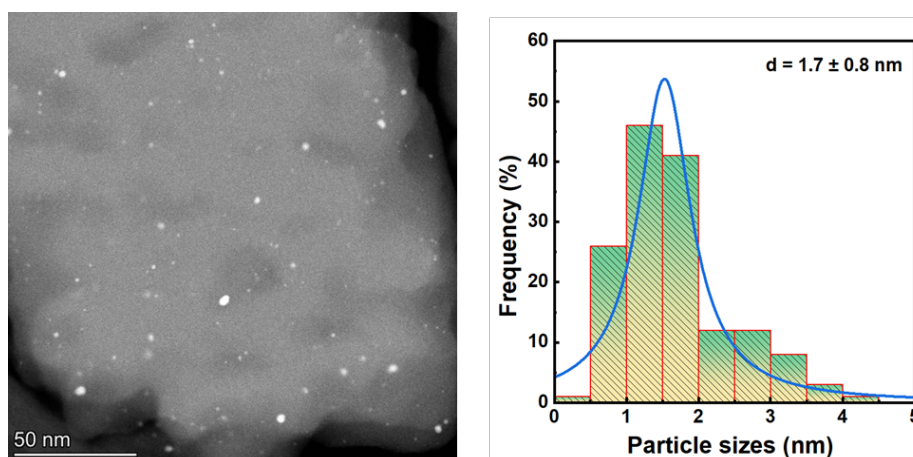


Figure R9. Pt dispersion of spent Pt@Sn-MFI after three regeneration cycles. **a**, HAADF-STEM image. **b**, Corresponding cluster size distribution.

The related change is described in the revised manuscript as below.

Given the importance of catalyst reusability, we further evaluated its regeneration performance. As shown in Supplementary Fig. 11, after three regeneration cycles, the catalyst retained approximately 89.9% of its initial propane conversion while maintaining a high propylene selectivity of 99.7%. The HAADF-STEM image of spent Pt@Sn-MFI after three regeneration cycles showed that the majority of Pt species remained as clusters smaller than 2 nm in size (Supplementary Fig. 12), indicating minimal sintering and exceptional structural stability.

Comments 6: *The substrates in the propane dehydrogenation reaction are relatively small molecules. The mass transfer difference should not be the reason (Page 9-10, line 279-280).*

Response: We sincerely appreciate the reviewer's insightful comment. While we agree that the substrates involved in propane dehydrogenation, such as propane and propylene, are relatively small molecules, diffusion constraints within the microporous structures of zeolites can still significantly impact catalytic performance. Some studies have demonstrated that the inherent micropores of zeolites can impose significant restrictions on the diffusion of propylene, particularly under reaction conditions, where the accumulation of propylene in these confined spaces promotes coke formation.¹ This phenomenon deteriorates catalytic performance and accelerates deactivation. To address this, many researchers have explored the introduction of mesopores into zeolite frameworks, thereby alleviating diffusion constraints and enhancing catalytic stability.² Therefore, even for small molecules like propane and propylene, diffusion limitations within zeolite micropores can play a crucial role in catalyst deactivation during PDH reactions.

Comments 7: *Why did the authors use two kinds of TPAOH solution with different concentrations during the synthesis of MFI related catalysts? The authors are suggested to discuss the reason why the introduction of Sn source into the synthesis of*

MFI zeolite helped to create more defective sites or mesopores and cite some references.

How was the defect-free Pt@Sn-MFI synthesized?

Response: We appreciate the reviewer's comments. Regarding the use of two different concentrations of TPAOH in the synthesis of MFI-related catalysts, the selection was based on the works of Corma and co-workers^{3,4}. In this approach, the high-concentration TPAOH (i.e., 40 wt%) did not contain K, while the low-concentration TPAOH (i.e., 20 wt%) contained K. Using these two different concentrations can adjust the K content, which in turn promoted the dispersion of Pt species on the zeolite support. However, our ICP analysis revealed that the final catalysts contained only negligible K content (~0.04 wt%), likely due to the zeolite preparation process. We have clarified this in the revised manuscript.

Regarding the introduction of the Sn source into MFI zeolite synthesis, the incorporation of Sn as a tetrahedral species, substituting Si in the zeolite framework, can disrupt the regularity of the structure by interacting with Si species during the crystallization process. This interaction results in the formation of defect sites and mesopores⁵⁻⁷. We have expanded the discussion on this aspect in the revised manuscript, and appropriate references have been cited to support our explanations.

To synthesize defect-free Pt@Sn-MFI, we employed a modified hydrothermal synthesis method that minimizes the formation of framework defects by incorporating fluoride ions (F^-) into the synthesis gel. The F^- ions act as mineralizing agents, balancing the charge of organic structure-directing agents during zeolite crystallization, thereby reducing defect formation and leading to a more ordered framework^{8,9}. This approach had already been explored widely and always resulted in zeolites with no or rare connectivity defects^{8,10}. Specifically, the synthesis process as follows: 100 μ L of H_2PtCl_6 aqueous (0.44 mol L^{-1}) containing 18.6 mg of EDTA and 17.5 μ L of $SnCl_4$ aqueous containing 58.8 mg of EDTA were added to an aqueous mixture containing TPAOH solution with components of 3.69 g of 20 wt% TPAOH (Sigma-Aldrich, containing ~0.6 wt% of K) and 3.0 g of 40 wt% TPAOH (Alfa-Aesar without K), 5.6 g of tetraethyl orthosilicate, 0.35 g of HF, and 0.08 g of seeds. The resulting solution was

stirred, transferred to a Teflon-lined autoclave, and crystallized at 170 °C for 7 days. The obtained crystals were filtered, washed, and dried, followed by reduction under 10 vol% H₂ in Ar at 550 °C for 2 h to obtain the defect-free Pt@Sn-MFI. We have included the synthesis procedure in the revised manuscript.

The related change is described in the revised manuscript as below.

The content of K in MFI is negligible, approximately 0.04 wt%, which is different previous work^{12,51}, likely attributed to the different procedure of zeolite preparation.

...the introduction of Sn into the synthetic gel significantly disrupts the regularity of the MFI structure by interacting with Si species during the crystallization process, resulting in the formation of disordered mesopores.

Synthesis of defect-free PtSn/MFI. *The defect-free Pt@Sn-MFI was prepared by a modified hydrothermal synthesis method that minimizes the formation of framework defects by incorporating fluoride ions (F⁻) into the synthesis gel. Typically, 100 µL of H₂PtCl₆ aqueous (0.44 mol L⁻¹) containing 18.6 mg of EDTA and 17.5 µL of SnCl₄ aqueous containing 58.8 mg of EDTA were added to an aqueous mixture containing TPAOH solution with components of 3.69 g of 20 wt% TPAOH (Sigma-Aldrich, containing ~0.6 wt% of K) and 3.0 g of 40 wt% TPAOH (Alfa-Aesar without K), 5.6 g of tetraethyl orthosilicate, 0.35 g of HF, and 0.08 g of seeds. The resulting solution was stirred, transferred to a Teflon-lined autoclave, and crystallized at 170 °C for 7 days. The obtained crystals were filtered, washed, and dried, followed by reduction under 10 vol% H₂ in Ar at 550 °C for 2 h to obtain the defect-free Pt@Sn-MFI.*

Comments 8: *Since there are numerous Si-OH groups in MFI structure, the contribution of silanol groups to this band at 957 cm⁻¹ in Fig. 2c must be eliminated, by a pretreatment under vacuum at elevated temperature.*

Response: We appreciate this valuable suggestion. If we understand correctly, the reviewer is referring to Fig. 1c rather than Fig. 2c. The data in Fig. 1c were obtained using ATR-FTIR, and due to the exposure of the sample to air during the measurement,

completely eliminating the contribution of silanol groups at 957 cm^{-1} is difficult, even with vacuum pretreatment at elevated temperatures. This limitation is inherent to the ATR-FTIR setup used in our study. Moreover, our characterization results from XRD, UV-Vis, XPS, and ^{119}Sn -NMR provide strong and consistent evidence for the isomorphous substitution of Sn in the MFI framework, further supporting the validity of our findings. Therefore, in light of this, and to avoid potential confusion, we have decided to remove Fig. 1c and its related discussion from the manuscript.

Comments 9: *Please provide the XRD pattern of the sample with Sn/Pt ratio of 6, because too much Sn may hinder the crystallization of MFI structure (Page 9, line 263-266). The authors should provide proofs for the existence of extra-framework Sn (Page 9, line 270-271).*

Response: We appreciate this valuable suggestion. Following the reviewer's comments, we have added the XRD pattern of the sample with a Sn/Pt ratio of 6 (i.e., Pt@Sn-MFI_6), now presented in Figure R10a. Compared to Pt@Sn-MFI_3, the Pt@Sn-MFI_6 with higher Sn content showed significantly weaker diffraction peaks corresponding to the MFI, indicating its poor crystallinity structure. This observation supports the conclusion that excessive Sn loading hinders the crystallization of the MFI structure.

To further confirm the existence of extra-framework Sn species, we have included the UV-Vis spectrum of Pt@Sn-MFI_6 (Figure R10b). In addition to the characteristic absorption bands of framework Sn species (200-250 nm), distinct absorption features associated with extra-framework Sn were observed, including oligomeric Sn species (250 – 350 nm) and larger Sn aggregates (>450 nm)^{11,12}. Furthermore, imaging characterization of Pt@Sn-MFI_6 revealed the presence of a PtSn alloy (Figures R10c-e), providing direct evidence of extra-framework Sn species. These results collectively confirm the existence of extra-framework Sn.

We have added these discussions in the revised manuscript and placed the new results in Supplementary Fig. 8.

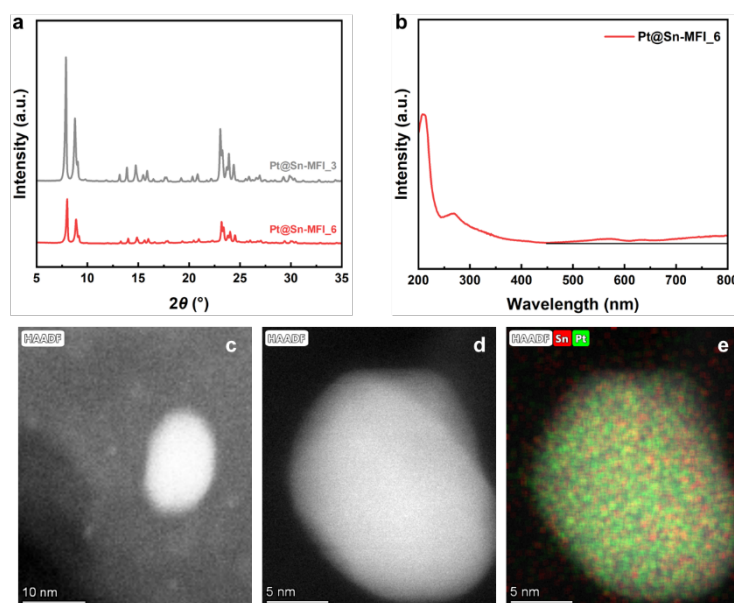


Figure R10. Structural characterization of Pt@Sn-MFI_6. **a**, XRD patterns. **b**, DR UV-Vis spectrum. **c-d**, HAADF-STEM images. **e**, EDS-Mapping.

The related change is described in the revised manuscript as below.

This decline in conversion may be attributed to poor crystallinity of the MFI structure (Supplementary Fig. 8a) and excessive Sn (e.g., extra-framework Sn species, as indicated by DR UV-Vis, HAADF-STEM image and EDS-Mapping in Supplementary Figs. 8b-e) partially covering active Pt sites...

Comments 10: SEM images can not provide the proofs for the existence of mesopores (Page 5, line 145-146). Pt was not proved to be confined inside the pore channels of MFI structure (Page 6, line 148-149). The TEM technique provides only a projection of a specific crystal plane and cannot conclusively prove that these Pt species are located within the MFI structure. (Page 7, line 188-190)

Response: We appreciate this valuable suggestion and apologize for any misunderstanding caused by our previous description. We acknowledge that SEM images cannot directly confirm the presence of mesopores. Instead, they reveal the

increased surface roughness of Sn-containing zeolites, which suggests structural irregularities induced by the interaction between Sn and Si species during synthesis. This disruption in structural regularity may contribute to the formation of mesopores, which are further verified by additional characterization techniques, such as N₂ adsorption-desorption isotherms and (S)TEM imaging. We have reworded this point in the revised manuscript to avoid any confusion.

Regarding the confinement of Pt within the pores of the MFI structure, we respectfully disagree with the assertion that this cannot be proven. The confinement of Pt within the pores leads to partial pore blockage, which consequently reduces the available surface area¹³. This phenomenon has been well-documented in the literatures by esteemed research groups, such as Jihong Yu^{14,15}, Dongyuan Zhao¹⁶ and Avelino Corma¹⁷, further supporting our claim.

While we acknowledge that TEM provides only a projection of a specific crystal plane, it is important to highlight that no Pt nanoclusters were observed at the edges of the zeolite crystals in our (S)TEM images. When considered alongside N₂ physisorption measurements, which indicate changes in textural properties, it is reasonable to conclude that Pt nanoclusters are confined within the MFI structure.

We have clarified these points in the revised manuscript.

The related change is described in the revised manuscript as below.

The resulting structural irregularity was reflected in the rougher morphology of Sn-containing zeolites, as observed in SEM images (Supplementary Fig. 1), while the presence of disordered mesopores was further confirmed by subsequent (S)TEM analysis. In addition, the slightly lower specific surface area of Pt@Sn-MFI compared to Sn-MFI, along with subsequent (S)TEM images, suggests that...

However, in HAADF-STEM images (Figs. 2e-g), no Pt nanoclusters were observed at the edges of the zeolite crystals. Instead, ultrafine Pt clusters with an average size of 1.1 nm were observed in areas away from the crystal edges, confined within the

wormhole-type hierarchical pores of the MFI zeolite (indicated by the red area in Figs. 2e-f).

Comments 11: *Why did the EDTA-Sn complex enhance the NMR selectivity? What is the meaning of selectivity here? (Page 6, line 165-166)*

Response: We sincerely appreciate the reviewer's insightful question. The term "NMR selectivity" (should be "NMR sensitivity" if we understand right) in this context refers to the ability to enhance the detection of framework Sn species in ^{119}Sn MAS NMR spectra. One of the primary challenges in using ^{119}Sn MAS NMR for zeolite characterization is its low sensitivity, which arises from two key factors of low Sn content in the zeolite framework (up to 2 wt%)¹⁸ and low natural abundance of the ^{119}Sn isotope (8.59%)⁷. Additionally, ^{119}Sn exhibits a long relaxation time (T_1), making it impractical to simply increase the number of scans to compensate for low signal intensity¹⁹.

To address these limitations, we employed an EDTA- ^{119}Sn complex as the Sn precursor in the synthesis of ^{119}Sn -enriched Pt@Sn-MFI, which significantly improved the NMR signal sensitivity. This approach enables more reliable detection and analysis of framework Sn species within the zeolite structure^{7,20}.

We have clarified this point in the revised manuscript.

The related change is described in the revised manuscript as below.

Enhanced NMR sensitivity was achieved by synthesizing ^{119}Sn -enriched Pt@Sn-MFI using an EDTA- ^{119}Sn complex as the Sn precursor⁴⁷.

Comments 12: *How did the authors calculate the propene yield? It is supposed to be 59%? (Page 9, line 259)*

Response: We appreciate this valuable comment. The propene yield was calculated using the following formula:

$$\text{Propene Yield (\%)} = \text{Propane Conversion (\%)} \times \text{Propene Selectivity (\%)} / 100$$

After carefully re-evaluating our data, we confirm that the correct propene yield should be 58.7%, and we have checked and revised the manuscript accordingly. Thank you for pointing this out.

Comments 13: *The difference among the three samples in Supplementary Fig. 11 can be ignored. The authors may monitor the C₃H₆-desorption experiment through in-situ DRIFTS.*

Response: We appreciate the reviewer's valuable suggestion. Following this recommendation, we conducted *in-situ* DRIFTS experiments to monitor C₃H₆ desorption. The newly obtained *in-situ* DRIFTS results (Figure R11) reveal distinct differences in propylene desorption behavior among the three catalysts. Specifically, Pt@Sn-MFI exhibited faster propylene desorption compared to both PtSn/MFI and Pt@MFI, clearly demonstrating weaker propylene adsorption on the Pt@Sn-MFI catalyst. This observation provides experimental evidence supporting our hypothesis that the unique structure of Pt@Sn-MFI leads to reduced propylene adsorption strength, which correlates with its enhanced propylene selectivity and catalyst longevity. We have removed the original Supplementary Fig. 11 and replaced it with the new experimental data (now included as Supplementary Fig. 16) and corresponding discussion in the revised manuscript

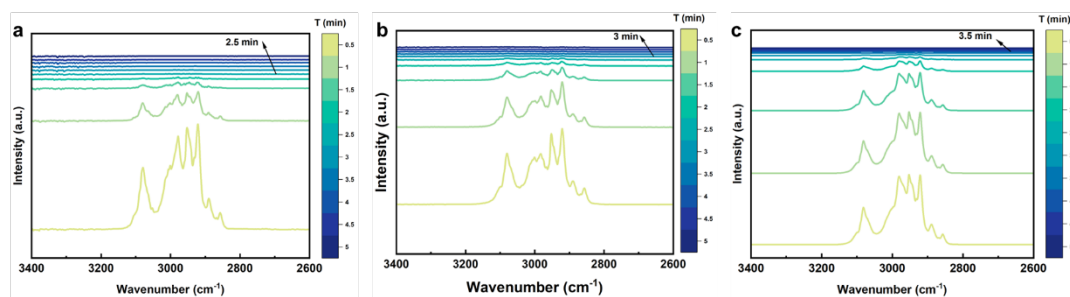


Figure R11. *In-situ* DRIFTS experiment to monitor C₃H₆ desorption. **a**, Pt@Sn-MFI. **b**, PtSn/MFI. **c**, Pt@MFI.

The related change is described in the revised manuscript as below.

This is corroborated by faster propylene desorption observed by in-situ DRIFTS spectra of C₃H₆-desorption experiments on Pt@Sn-MFI (Supplementary Fig. 16).

Comments 14: *The authors should indicate the meaning of color and the arrows in Fig. 5a and c.*

Response: We appreciate the reviewer's valuable suggestion. In the revised manuscript, we have added descriptions for the colors and arrows in Figs. 5a and 5c. Specifically, black arrows indicate increased signals, while purple arrows represent decreased signals.

Comments 15: *The authors should provide more detail information for the in-situ DRIFTS with CD₃CN as the probe molecules, including the temperature and duration of the adsorption and desorption process.*

Response: We appreciate the reviewer's valuable suggestion. The details of *in-situ* DRIFTS using CD₃CN as the probe molecule are as follows: The DRIFTS spectra were recorded on a Thermo Scientific Nicolet 6700 spectrometer. Typically, the sample was pre-treated at 350 °C under He flow for 3 h to desorb water and volatile compounds. After cooling the sample to the desired temperatures (i.e., 30 and 100 °C), the background spectra were recorded at these temperatures. Then, the sample was exposed to CD₃CN by bubbling at room temperature for 15 min until saturation. Afterward, the sample was heated to the desired temperature and maintained for 30 min before measurement. Spectra were recorded after 10 min at each temperature, with 32 scans and a resolution of 4 cm⁻¹.

We have added the corresponding details in the revised manuscript.

The related change is described in the revised manuscript as below.

For in-situ CD₃CN-adsorbed DRIFTS, the sample was pre-treated at 350 °C under He flow for 3 h to desorb water and volatile compounds. After cooling the sample to

the desired temperatures (i.e., 30 and 100 °C), the background spectra were recorded at these temperatures. The sample was then exposed to CD₃CN by bubbling at room temperature for 15 min until saturation followed by heating to the target temperature and maintaining for 30 min before measurement. Spectra were recorded after 10 min at each temperature, with 32 scans and a resolution of 4 cm⁻¹.

Comments 16: The complete of TPAOH under H₂/N₂ flow should be confirmed by TG analysis.

Response: We appreciate the reviewer's valuable comments. Following the reviewer's suggestion, we have conducted a TGA experiment to track the weight variations of the as-synthesized Pt@Sn-MFI under a 4% H₂/Ar flow as a function of temperature. The obtained TGA results showed that the decomposition and elimination of TPAOH occurred at temperatures below 500 °C (Figure R12), confirming that TPAOH could be effectively eliminated under our employed conditions of 550 °C for 2h. Considering that our result align with previous reports on metal@zeolite catalysts synthesized via similar ligand-protected one-pot hydrothermal methods followed by direct H₂ reduction^{14,15}, we decided not to include this result in the manuscript but present it here for review purpose only.

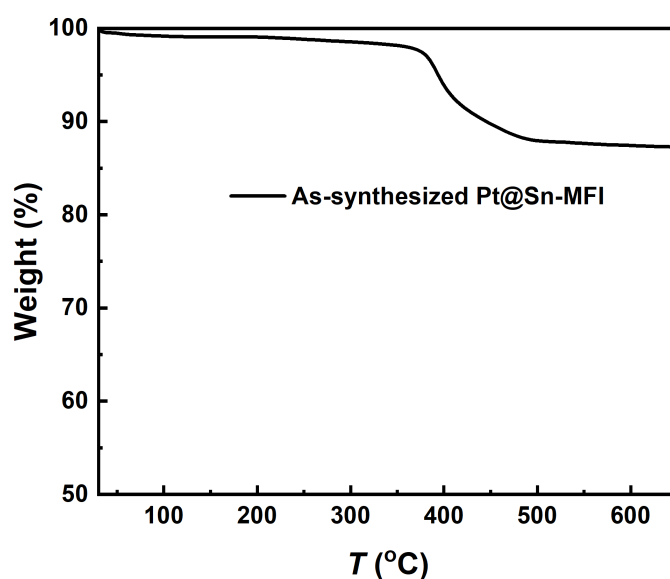


Figure R12. TGA curve of the as-synthesized Pt@Sn-MFI under a 4%H₂/Ar flow.

Comments 17: The intensities of the CO adsorbed IR spectra in Figure 3d should be provided.

Response: We appreciate the reviewer's valuable comments. Following the reviewer's suggestion, we have provided the intensities of the CO-adsorbed IR spectra in Figure 3d in the revised manuscript.

Reviewer #2 (Remarks to the Author):

Comments 1: *In the manuscript titled “Highly Efficient Catalytic Propane Dehydrogenation Driven by MFI Zeolite Defect Sites,” the researchers synthesized a pure siliceous zeolite MFI-supported Pt-Sn catalyst using a modified ligand-protected one-pot hydrothermal method. This catalyst demonstrated a propylene selectivity of over 98.5% at a gas hourly space velocity of $9600 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and 550°C , maintaining stability for at least 120 hours. Additionally, the authors employed various characterization techniques, isotope-labeled experiments, and DFT calculations to identify the active sites on the catalyst and elucidate the reaction mechanism of propane dehydrogenation (PDH). The direction taken by the authors is intriguing, and the development of efficient catalysts for propane dehydrogenation is undoubtedly significant for the chemical industry.*

However, the reviewer has expressed concerns regarding the characterization of the catalysts. Before further consideration, the authors should address these concerns as outlined below:

Response: We sincerely appreciate the reviewer for her/his appreciation of our work and insightful comments. We have carefully revised our manuscript following the valuable suggestions.

Comments 2: *The authors identified the $[\text{SiO}]_3\text{-Sn-O-Ptn}$ as the active sites for the Pt@Sn-MFI catalyst, citing reference 23 for support (J. Catal. 397, 44-57 (2021)). Do the authors have additional references that could support this chemical structure? What are the differences between the catalyst described in this manuscript and the one in reference 23? In other words, what accounts for the superior PDH performance of the catalyst developed in this work compared to previous investigations, such as reference 23?*

Response: We appreciate the reviewer for raising this important point. In addition to reference 23 (J. Catal. 397, 44–57 (2021)), several other very recent studies have reported a similar chemical structure, where framework-Sn anchors Pt sites in Pt-Sn

catalysts for PDH^{21,22}, further supporting our proposed active site. We have now included additional relevant references in the revised manuscript to strengthen this discussion.

Regarding the comparison with the catalyst in reference 23, there are several key differences in catalyst composition, preparation, and PDH performance:

- 1) **Support Material:** Our study employs a worm-like MFI zeolite, whereas reference 23 uses a Beta zeolite support. The structural and textural differences between these supports influence metal dispersion and catalytic behavior.
- 2) **Synthesis Method:** We synthesized Pt@Sn-MFI using a one-step hydrothermal method, while reference 23 employed a more complex multi-step synthesis for Pt/Sn-Beta. Our approach ensures better control over metal incorporation and dispersion.
- 3) **Sn Oxidation State and Pt-Sn Interaction:** Although both catalysts feature Sn-anchored Pt sites within the zeolite framework, our characterization results reveal that Sn species in Pt@Sn-MFI are predominantly in the +4 oxidation state, with no evidence of metallic Sn (i.e., no PtSn alloy formation). In contrast, reference 23 reports Sn species primarily in the +2 state, along with the presence of metallic Sn. This distinction impacts catalyst stability and selectivity.
- 4) **Reaction Conditions and Stability:** Our catalyst evaluation was carried out under relatively harsh reaction conditions, with a higher reaction temperature and propane partial pressure (550 °C and 10% C₃H₈ in N₂), whereas reference 23 used milder reaction conditions (500 °C and 5% C₃H₈ in N₂). Despite these harsher conditions, the inverse deactivation coefficient of Pt@Sn-MFI remains comparable to that in reference 23, highlighting its good stability. Furthermore, our newly added long-term PDH test under near-industrial conditions showed continuous operation for 80 h without deactivation (Figure R13), underscoring its robustness. The HAADF-STEM analysis of the spent Pt@Sn-MFI catalyst following the pure propane dehydrogenation experiment showed that the Pt nanoclusters retained their structure without noticeable aggregation (Figure R14), highlighting the catalyst's excellent anti-sintering properties.

These differences collectively contribute to the superior PDH performance of Pt@Sn-MFI, particularly in terms of catalyst longevity and resistance to sintering. We have added these discussions in the revised manuscript and placed the new results in Supplementary Figs. 9 and 10.

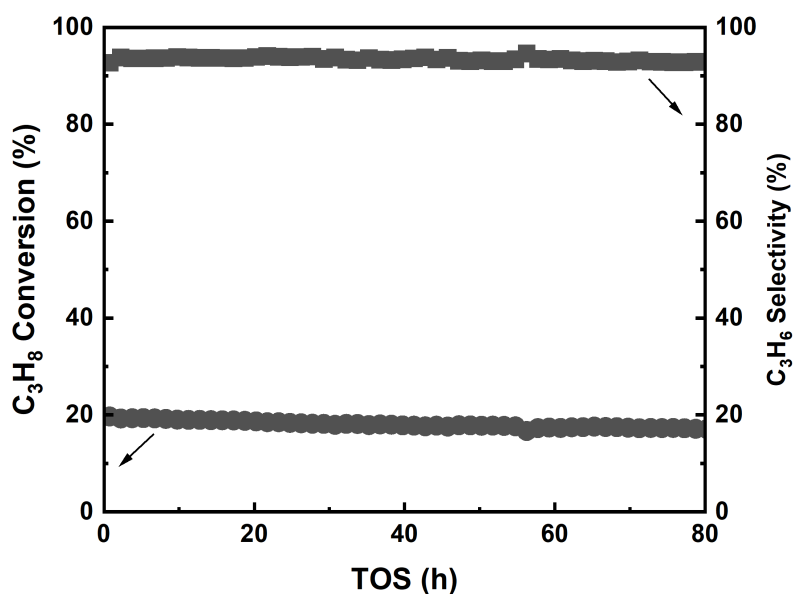


Figure R13. Stability evaluation of the Pt@Sn-MFI catalyst for the dehydrogenation of pure propane. Reaction conditions: $T = 550\text{ }^{\circ}\text{C}$, pure C_3H_8 , $GHSV = 9600\text{ mL g}_{\text{cat}}^{-1}\text{h}^{-1}$.

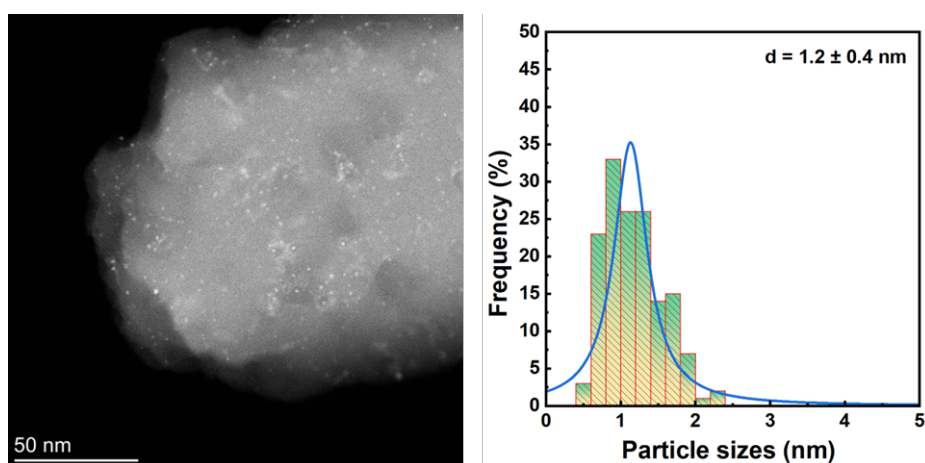


Figure R14. Pt dispersion of spent Pt@Sn-MFI catalyst under pure propane flow. **a**, HAADF-STEM image. **b**, Corresponding Pt cluster size distribution.

The related change is described in the revised manuscript as below.

Additionally, the stability of the Pt@Sn-MFI catalyst was assessed under near-industrial reaction conditions (i.e., $T = 550\text{ }^{\circ}\text{C}$, pure C_3H_8 , $\text{GHSV} = 9600\text{ mL g}_{\text{cat}}^{-1}\text{h}^{-1}$), as well. As shown in Supplementary Fig. 9, the Pt@Sn-MFI catalyst exhibited no significant signs of deactivation over 80 h of continuous operation. The HAADF-STEM image and corresponding Pt cluster size dispersion of the spent Pt@Sn-MFI catalyst following the pure propane dehydrogenation experiment showed no obvious aggregation of the Pt nanoclusters (Supplementary Fig. 10), demonstrating their robust structure and excellent anti-sintering properties.

Comments 3: *The authors employed ex-situ X-ray absorption spectroscopy (XAS) to determine the structural details of Pt. However, Pt species have the potential to oxidize in air (ACS Catal. 9, 10626-10639 (2019)), making in-situ XAS experiments more reliable (Nat. Catal. 4, 453–456 (2021)). Additionally, conducting in-situ experiments for Sn K-edge XANES and Sn K-edge EXAFS spectra would also help identify the chemical structure of the Sn element (ACS Catal. 14, 2859-2871 (2024)).*

Response: We appreciate the reviewer for raising this point. We fully acknowledge that *in-situ* XAS provides more direct insights into the electronic and coordination environment of Pt and Sn species under reaction conditions. However, due to experimental constraints, we were unable to perform *in-situ* XAS measurements in this study.

Despite this limitation, our *ex-situ* XAS results, combined with complementary techniques such as XRD, DR UV-Vis, *quasi-in-situ* XPS, ^{119}Sn MAS NMR, and *in-situ* DRIFTS, provide strong evidence for the structural and electronic properties of both Pt and Sn species. Furthermore, our observations are in line with previous studies (e.g., ACS Catal. 14, 2859-2871 (2024)).

We acknowledge this limitation in the revised manuscript, and we will explore opportunities to focus on *in-situ* XAS investigations to further elucidate the dynamic structural evolution of Pt and Sn species under reaction conditions.

Comments 4: *The captions for Supplementary Fig. 10 c and d are missing.*

Response: We appreciate the reviewer for raising this point. In the revised Supplementary Information, we have added the missing captions for Supplementary Figs. 10c and 10d (now presented as Supplementary Figs. 15c and 15d) to ensure clarity and completeness.

Comments 5: *The authors compared the PDH performance of Pt@Sn-MFI (Con. 59.2% & Sel. 98.5%) with that of PtSn/MFI (Con. 58.3% & Sel. 98.2%) synthesized using the traditional impregnation method. However, the performance of Pt@Sn-MFI does not appear to be significantly better. The authors should provide a more detailed discussion on the differences between the Pt@Sn-MFI catalysts and the traditional PtSn/MFI catalysts.*

Response: We appreciate the reviewer for raising this point. While the C₃H₈ conversion and C₃H₆ selectivity of Pt@Sn-MFI (59.2% & 98.5%) and PtSn/MFI (58.3% & 98.2%) appear similar under initial reaction conditions, the key advantages of Pt@Sn-MFI lie in its enhanced stability and resistance to deactivation. Specifically, during 12 h of continuous operation, Pt@Sn-MFI maintained a stable C₃H₈ conversion of 59.2%, whereas PtSn/MFI showed a noticeable decline from 58.3% to 52.8%, indicating its higher susceptibility to deactivation.

To further clarify these distinctions, we have expanded the discussion in the revised manuscript.

The related change is described in the revised manuscript as below.

Notably, although the C₃H₈ conversion and C₃H₆ selectivity of Pt@Sn-MFI (59.2% & 98.5%) and PtSn/MFI (58.3% & 98.2%) appear similar under initial reaction conditions, the key advantages of Pt@Sn-MFI lie in its enhanced stability and resistance to deactivation. Specifically, during 12 h of continuous operation, Pt@Sn-MFI maintained a stable C₃H₈ conversion of 59.2%, whereas PtSn/MFI showed a noticeable decline from 58.3 to 52.8%, indicating its higher susceptibility to

deactivation.

Comments 6: *One highlight of the Pt@Sn-MFI catalyst is its extremely high stability in PDH while maintaining a high selectivity for propylene and conversion. However, the authors did not provide sufficient experimental results to support the reasons behind this catalyst's enhanced PDH stability. What is the relationship between the chemical structure of Pt@Sn-MFI and its high stability?*

Response: We appreciate the reviewer for raising this point. The exceptional stability of Pt@Sn-MFI in PDH is primarily attributed to its unique and robust $[\text{SiO}]_3\text{-Sn-O-Pt}_n$ structure within worm-like MFI zeolite, which enhances Pt dispersion (Figs. 2b-f, Figs. 3a-c and Supplementary Figs. 2). This high dispersion increases the availability of active Pt sites while effectively suppresses side reactions, such as structure-sensitive C-C cracking and coke deposition.²³ The strong interaction between Sn and Pt modifies the electronic environment of Pt (Figs. 3a-d and Supplementary Fig. 4), weakens the bonds of Pt-(C-C-C) and repels adsorbed propylene, thereby enhancing propylene selectivity and suppressing coke formation (Supplementary Figs. 15-17). Furthermore, the confinement effect of the wormhole-type MFI zeolite framework helps stabilize Pt species within the channels (Figs. 3e-f), reducing their mobility and aggregation, even under near-industrial reaction conditions and repeated dehydrogenation-oxidative regeneration cycles (Figs. 2d-f and R13-16). These structural advantages collectively contribute to its high stability.

To directly support the correlation between structure and stability, we have now included additional stability tests under near-industrial reaction conditions (Fig. R13) and dehydrogenation-oxidative regeneration cycle tests (Fig. R15), along with their complementary imaging analyses (Figs. R14 and R16) in the revised manuscript. These new results further confirm the robustness of $[\text{SiO}]_3\text{-Sn-O-Pt}_n$ structure within worm-like MFI zeolite. We have added these discussions in the revised manuscript and placed the new results in Supplementary Figs. 9-12.

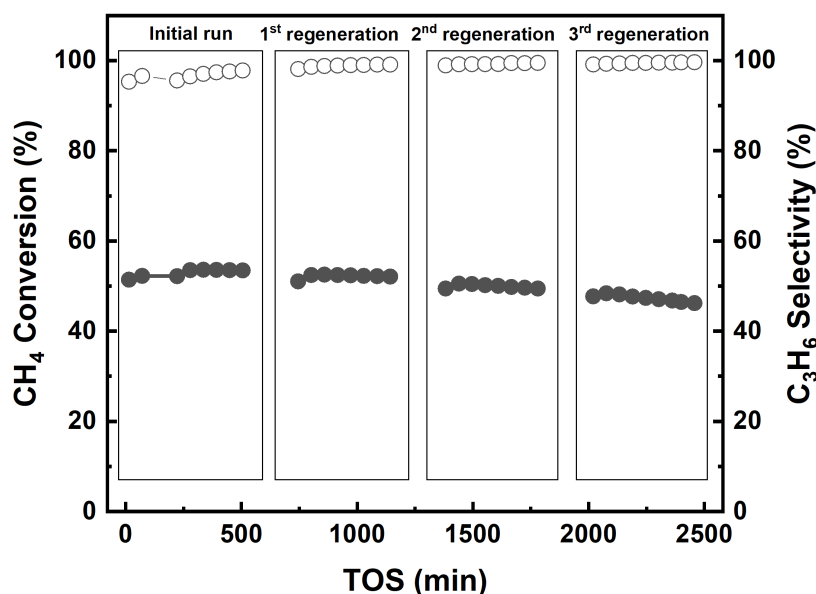


Figure R15. Dehydrogenation-oxidative regeneration test over the Pt@Sn-MFI catalyst. Reaction conditions were as follows: 1 bar, 550 °C, GHSV = 15000 mL g_{cat}⁻¹ h⁻¹. Regeneration conditions were as follows: 500 °C in air atmosphere for 30 min and subsequent 550 °C in H₂ for 1 h.

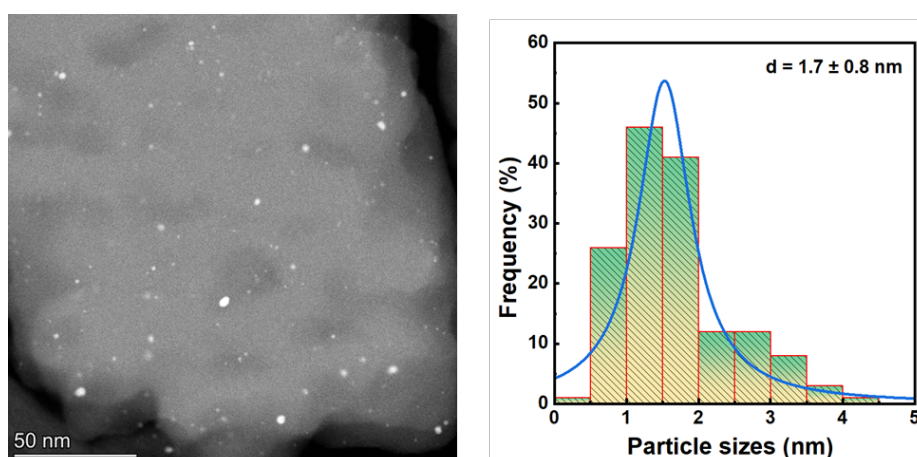


Figure R16. Pt dispersion of spent Pt@Sn-MFI after three regeneration cycles. **a**, HAADF-STEM image. **b**, Corresponding cluster size distribution.

The related change is described in the revised manuscript as below.

The unique and robust [SiO]₃-Sn-O-Pt_n structure in the worm-like Pt@Sn-MFI remarkably improves the propane conversion and propylene selectivity, attributed to the geometric and electronic effects of Sn. The small-sized Pt clusters not only provide more available active Pt sites but also effectively suppress side reactions, such as

structure-sensitive C–C cracking and coke deposition.¹ Simultaneously, Sn contributes by donating electrons to Pt, which weakens the bonds of Pt-(C-C-C) and repels adsorbed propylene, thereby enhancing propylene selectivity.

Additionally, the stability of the Pt@Sn-MFI catalyst was assessed under near-industrial reaction conditions (i.e., $T = 550\text{ }^{\circ}\text{C}$, pure C_3H_8 , $\text{GHSV} = 9600\text{ mL g}_{\text{cat}}^{-1}\text{h}^{-1}$), as well. As shown in Supplementary Fig. 9, the Pt@Sn-MFI catalyst exhibited no significant signs of deactivation over 80 h of continuous operation. The HAADF-STEM analysis of the spent Pt@Sn-MFI catalyst following the pure propane dehydrogenation experiment showed that no obvious aggregation of the Pt nanoclusters (Supplementary Fig. 10), demonstrating their robust structure and excellent anti-sintering properties.

Given the importance of catalyst reusability, we further evaluated its regeneration performance. As shown in Supplementary Fig. 11, after three regeneration cycles, the catalyst retained approximately 89.9% of its initial propane conversion while maintaining a high propylene selectivity of 99.7%. The HAADF-STEM image of spent Pt@Sn-MFI after three regeneration cycles showed that the majority of Pt species remained as clusters smaller than 2 nm in size (Supplementary Fig. 12), indicating minimal sintering and exceptional structural stability.

Comments 7: *Comparing the activities of the Pt@Sn-MFI catalysts with those of Pt and PtSn catalysts reported in the literature is challenging due to variations in temperature, propane partial pressure, hydrogen partial pressure, propane conversion, and the approach to equilibrium in each study. It would be more appropriate to compare the performance based on the apparent forward rate coefficient for PDH, as suggested in references such as ACS Catal. 14, 3986-4000 (2024).*

Response: We appreciate the reviewer for raising this point. We agree that comparing catalytic activities across different studies can be challenging due to variations in experimental conditions, such as temperature, propane and hydrogen partial pressures, and the approach to equilibrium. Following the suggestion, we have calculated and

compared the apparent forward rate coefficient for PDH based on the methodology from ACS Catal. 14, 3986-4000 (2024). Our analysis shows that the Pt@Sn-MFI catalyst exhibited an impressive apparent forward rate coefficient of $1224.9 \text{ mol}_{\text{C}_3\text{H}_6} \text{ g}_{\text{Pt}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ at 550 °C, surpassing the majority of state-of-the-art Pt-based catalysts. We have included this result and the corresponding discussion in both the revised Manuscript and revised Supporting Information. We have added these discussions in the revised manuscript and placed the new results in Supplementary Table 2. Additionally, considering the importance of the literature mentioned by the reviewer to our work, we have appropriately cited it in the revised manuscript.

The related change is described in the revised manuscript as below.

Considering the challenges of comparing catalytic activities across different studies due to variations in experimental conditions (e.g., temperature, propane partial pressures, and approach to equilibrium),²⁵ all catalysts were compared based on the PDH apparent forward rate coefficient. The results in Supplementary Table 2 showed that Pt@Sn-MFI exhibited an impressive apparent forward rate coefficient of $1064.5 \text{ mol}_{\text{C}_3\text{H}_6} \text{ g}_{\text{Pt}}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ at 550 °C.

Reviewer #3 (Remarks to the Author):

Comments 1: *The manuscript designed a robust Pt@Sn-MFI catalyst for efficient propane dehydrogenation (PDH) to propylene by engineering defect sites within the MFI zeolite framework. This work proposes a novel hydroxyl-assisted PDH reaction mechanism, underpinned by extensive experimental characterization and density functional theory (DFT) calculations. The findings highlight the synergistic role of Pt sites within the defect-rich Sn-MFI structure, facilitating selective C-H activation and stability. Overall, the manuscript is well-structured and methodologically rigorous. However, minor revisions are recommended before publication in Nature Communications. The detailed suggestions are listed below:*

Response: We sincerely appreciate the reviewer for her/his appreciation of our work and insightful comments. We have carefully revised our manuscript following the valuable suggestions.

Comments 2: *The abstract contains detailed information that could be condensed to more directly emphasize the most impactful findings.*

Response: We appreciate the reviewer for the insightful comments. Following the suggestion, we have condensed the abstract to emphasize the key findings more directly.

Comments 3: *It is generally understood that PtSn alloy is often considered the active site for catalyzing PDH. Could the authors clarify why Sn does not form an alloy with Pt in the Pt@Sn-MFI catalyst, particularly given the proximity of Pt and Sn?*

Response: We appreciate the reviewer for the insightful comments. In the Pt@Sn-MFI catalyst, Sn was primarily incorporated into the zeolite framework as isolated Sn species rather than forming a PtSn alloy, as supported by DR UV-Vis, XPS, and ^{119}Sn NMR results. The strong interaction between Sn and the zeolite framework stabilizes Sn in an oxidized state, preventing its reduction and subsequent alloy formation with

Pt, even after interacting strongly with Pt species.¹³ We had clarified this point in the original manuscript.

The related change is described in the revised manuscript as below.

...nonmetallic Sn species were found in Pt@Sn-MFI, indicating that the strong interaction between Sn and the zeolite framework stabilizes Sn in an oxidized state, preventing its reduction and subsequent alloy formation with Pt, even after interacting strongly with Pt species.

Comments 4: *Please explain the advantages of the active site structure ([SiO]₃–Sn–O–Pt_n) in Pt@Sn-MFI compared to conventional PtSn alloys, especially in terms of catalytic performance.*

Response: We appreciate the reviewer for the insightful comments. The [SiO]₃–Sn–O–Pt_n structure in Pt@Sn-MFI offers significant advantages over conventional PtSn alloys as follows:

- 1) Pt clusters are highly dispersed and strongly anchored by integrated Sn sites, enhancing catalytic activity while suppressing sintering for improved stability.
- 2) This structure electronically modifies Pt, suppressing deep dehydrogenation and coke formation, thus improving propylene selectivity.
- 3) The confined environment within the worm-like MFI pores further stabilizes active Pt species and prevents their aggregation, ensuring sustained catalytic performance.

These collective effects contribute to the superior catalytic performance of Pt@Sn-MFI.

Comments 5: *In the figure legends for Figures 1 and 2, the specific modes used for the UV-Vis and IR spectra, respectively, are unclear. Clear labeling of these modes is suggested.*

Response: We appreciate the reviewer for the insightful comments. Following the

suggestion, we have clarified the specific modes used for the DR UV-Vis and ATR-FTIR spectra in the figure legends for Figures 1 and 2 in the revised manuscript.

Additionally, we recognize a potential issue with the data presented in Figure 1c of the original submission. As our ATR-FTIR measurements required sample exposure to air, the elimination of Si-OH species was challenging, which interfered with the detection of Si-O-Sn signals. Considering our characterization results from XRD, UV-Vis, *quasi-in situ* XPS, and ^{119}Sn -NMR provide strong and consistent evidence for the isomorphous substitution of Sn in the MFI framework, we have removed this dataset along with the corresponding discussion in the revised manuscript to maintain clarity and accuracy.

Comments 6: *It appears that phase correction has not been applied in Figures 3e and 3f. So, using $R+\alpha$ as the x-axis may not be accurate. Please re-evaluate the fitting process for these data to ensure accurate representation.*

Response: We appreciate the reviewer for the insightful comments. After carefully re-evaluating the fitting process for Figures 3e and 3f, we confirmed that phase correction was not applied. To avoid any misrepresentation, we have made modification in the revised manuscript.

Comments 7: *In Figures 4a–c, the performance data for different catalysts had been collected at different time points rather than at the same time points. Could the authors clarify the reason for this timing discrepancy?*

Response: We appreciate the reviewer for the insightful comments. The performance data for different catalysts in Figures 4a-c were collected at different time points due to the limitations of our experimental setup (4-channel Flowrence XD platform from Avantium), which sequentially measures the exhaust gases from each reaction tube using a single online gas chromatograph. Despite this, all catalysts were tested under

identical reaction conditions to ensure a valid comparison. We have added this clarification in the revised manuscript.

The related change is described in the revised manuscript as below.

...using a four-channel Flowrence XD platform from Avantium, equipped with an online gas chromatograph...

Comments 8: *The font clarity in Figures 5a and 5c should be improved for better readability.*

Response: We appreciate the reviewer for the insightful comments. Following your suggestion, we have improved the font clarity in Figures 5a and 5c to enhance readability in the revised manuscript.

Response References

- 1 Song, S. *et al.* Recent progress in metal-molecular sieve catalysts for propane dehydrogenation. *ACS Catalysis* **13**, 6044-6067 (2023).
- 2 Lu, J. *et al.* Pt-Zn clusters encapsulated in hierarchical MFI zeolite for efficient propane dehydrogenation. *Chemical Engineering Journal* **484**, 149369 (2024).
- 3 Liu, L., Lopez-Haro, M., Calvino, J. J. & Corma, A. Tutorial: structural characterization of isolated metal atoms and subnanometric metal clusters in zeolites. *Nature Protocols* **16**, 1871-1906 (2021).
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- 17 Bai, R. *et al.* Encapsulation of palladium carbide subnanometric species in zeolite boosts highly selective semihydrogenation of alkynes. *Angewandte Chemie International Edition* **62**, e202313101 (2023).
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- 19 Clayden, N. J., Dobson, C. M. & Fern, A. High-resolution solid-state tin-119 nuclear magnetic resonance spectroscopy of ternary tin oxides. *Journal of the Chemical Society, Dalton Transactions*, 843-847 (1989).
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Point-by-Point Responses to the Reviewers' Comments

Reviewer #1 (Remarks to the Author):

Comments 1: *The authors have addressed most of the issues in the revised manuscript; however, there are still problems regarding the construction of the theoretical calculation model, particularly concerning the catalytic centers. On one hand, the number of Sn atoms in a single MFI unit cell should consider the framework Si/Sn ratio. On the other hand, the number of Pt metal atoms in the catalytic center should take into account the results from TEM and EXAFS. Clearly, a catalytic center composed of three Pt metal atoms does not match either of these results. TEM shows that the particle size of the catalytic center is approximately 1.1 nm, which should be larger than the size of three Pt metal atoms. Additionally, the Pt-Pt coordination number (CN) is 6.7, inconsistent with the assumption of three atoms.*

Given these discrepancies, can this structural model truly reflect the catalytic reaction mechanism? Since one of the most important evidence for the hydroxy-assisted reaction in this study is derived from theoretical calculations, if the structural model itself is incorrect, can the results still be considered reliable?

Response: We sincerely appreciate the reviewer for the insightful comments regarding the rationality and accuracy of our theoretical calculation model, especially concerning the catalytic centers. Recognizing the validity of the reviewer's concerns, we have carefully reconsidered and reconstructed our structural model based as closely as possible on the experimental data:

(1) Regarding the Sn content in the MFI framework, the experimental ICP result showed a Si/Sn atomic ratio of 178, corresponding to an average Sn occupancy of around 0.5 Sn atom per MFI unit cell. In fact, atomic representation must involve integer numbers in catalysts, this low concentration implies an uneven distribution, **with some unit cells locally enriched in Sn atoms while others lack Sn entirely**. This interpretation aligns well with our DRIFTS, solid-state ^{119}Sn MAS NMR, and XAFS analyses, collectively confirming integrated Sn species as anchoring sites for Pt nanoclusters. Furthermore, the ICP measured Sn/Pt atomic ratio is 3.3, indicating that the Sn content is sufficient to stabilize the Pt nanoclusters. Therefore, in constructing our theoretical model, we first established Pt nanoclusters according to experimental Pt size measurements,¹ and Sn atoms were subsequently introduced one by one into the

optimized MFI framework to anchor the Pt clusters, followed by energy minimization principle until a structurally stable configuration representative of the catalytic system was achieved.

(2) Concerning the Pt nanocluster size, the reviewer correctly identified that a cluster composed of only three Pt atoms does not align with experimental observations. To resolve this discrepancy, we have revised our structural model based explicitly on combined STEM and EXAFS experimental results. STEM characterization indicates a Pt nanocluster size of approximately 1.1 nm, while EXAFS analysis shows a Pt-Pt coordination number of 6.7 and a bond distance of 2.76 Å. Accordingly, we constructed a stable four-layer Pt nanocluster containing 20 Pt atoms (Pt₂₀) with maximum Pt-Pt coordination number of 6 based on the previous literatures^[1]. This revised Pt₂₀ model (Figure R1), after structural optimization, exhibits a compact geometry with a diameter ~0.9 nm, closely matching the experimentally observations, thus significantly enhancing the realism of our computational model.

(3) To accommodate such a Pt nanocluster realistically, we also considered the hierarchical pore characteristics of our wormhole-like catalyst. Accordingly, several Si atoms were deliberately removed from the MFI framework in our computational model, creating sufficient internal space for the Pt₂₀ nanocluster. Such methodological adjustments are scientifically sound and commonly adopted in theoretical studies aiming to mimic realistic catalytic environments with hierarchical pore structures^[2,3].

(4) Most importantly, **recalculations of reaction pathways with the updated and experimentally validated structural model reconfirm the hydroxy-assisted reaction pathway as energetically favorable, with key reaction trends and conclusions unchanged** (Figure R2). Our updated calculations uphold the key conclusions presented in our manuscript, thus providing strong theoretical support consistent with experimental observations.

These modifications have been incorporated into the revised manuscript and supplementary materials (Supplementary Figure 21 and Figure 6). We believe that these adjustments address the reviewer's concerns effectively, enhancing the scientific robustness and reliability of our findings.

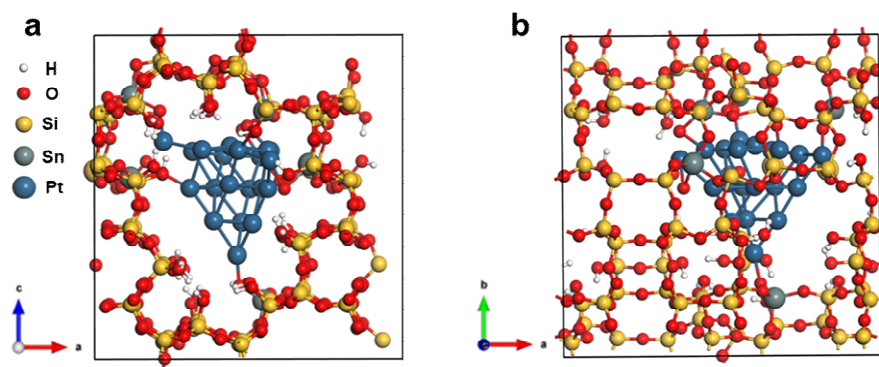


Figure R1. Stable structure of Sn doped into MFI framework bonding with Pt. a, View from the x-axis. **b,** View from the z-axis.

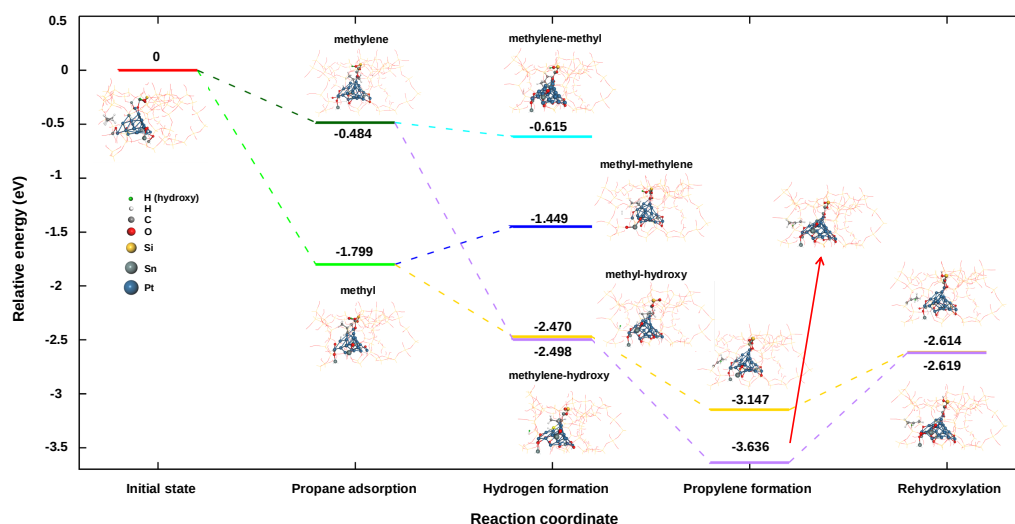


Figure R2. Reaction pathway of propane dehydrogenation. The values above the solid line represent the energy relative to the initial state (defined as zero). Specifically, in the initial state, free propane was confined within MFI channel. In the propane adsorption stage, the adsorption of the methyl (or methylene) group in propane on Pt sites was considered. In the hydrogen formation and desorption stage, hydrogen from propane's methyl and methylene groups, as well as from their combination (either methyl or methylene) with adjacent hydroxyl groups, was considered. In the propylene formation stage, the analysis focuses on two pathways (i.e., the methyl_hydroxyl and methylene_hydroxyl) that are considered more likely to occur in the reaction. In the rehydroxylation stage, H originating from propane on Pt sites spills over to adjacent unsaturated oxygen species, resulting in the regeneration of hydroxyl groups. The green,

white, grey, red, yellow, dimgrey and darkblue spheres represent H in hydroxyl, H in propane, C, O, Si, Sn, and Pt, respectively.

The related change is described in the revised manuscript as below.

A four-layer Pt nanocluster (Pt_{20}) was constructed based on the previous literature.⁶⁰ This cluster configuration yields a maximum Pt-Pt coordination number (CN) of 6 and a bond distance of 2.76 Å, which closely matches the experimentally EXAFS fitting data. Upon full relaxation, the Pt nanocluster retained a compact and thermodynamically stable geometry, exhibiting only minor deviations from the initial structure with fixed atomic positions. The final optimized nanocluster had a diameter of ~0.9 nm, closely matching the experimentally observed average cluster size of ~1.1 nm from STEM measurements, thereby validating the structural rationality of the model. Following the experimental guidance, Sn atoms were sequentially introduced into the optimized MFI framework as anchoring sites for the Pt nanoclusters. The entire system was then optimized using the energy minimization principle until a structurally stable model was achieved. Additionally, to realistically accommodate the Pt_{20} nanocluster within the catalyst's wormhole-like structure, several Si atoms were deliberately removed from the MFI framework and the remaining dangling bonds were saturated with hydroxyl groups, thus creating sufficient internal space for stable incorporation of the Pt nanocluster. This final optimized model ($Si_{61}O_{156}H_{32}Sn_6Pt_{20}$) exhibited high structural stability and accurately represented the catalytic system. Notably, the framework oxygen atoms coordinated to Sn were observed to play a critical role in stabilizing the Pt nanoclusters. This optimized structural model was then employed as the basis for subsequent mechanistic investigations, in which four distinct reaction pathways were systematically explored.

Reviewer #2 (Remarks to the Author):

Comments 1: *Although the authors addressed some of the comments, they were unable to conduct the in-situ XAS experiment due to "experimental constraints". This limitation compromises the quality and scientific contribution of the work.*

Response: We sincerely thank the reviewer for again emphasizing the importance of in-situ XAS characterization, and we fully acknowledge its value in elucidating detailed mechanistic insights by directly capturing real-time structural and electronic changes. Unfortunately, as explained previously, we faced practical constraints related to limited access to suitable synchrotron facilities and beam-time scheduling during the timeframe of this study.

To address this limitation comprehensively, we employed multiple complementary advanced characterization techniques, including XRD, DR UV-Vis, *quasi-in-situ* XPS, ^{119}Sn MAS NMR, in-situ DRIFTS using probe molecules (CO and CNCD_3) and ex-situ XAFS. Collectively, these techniques provided detailed and complementary information on chemical structures and electronic properties of the catalysts. For example, *quasi-in-situ* XPS clearly revealed electronic properties of both Pt and Sn species, which is consistent with previous literature^[4,5], while DR UV-Vis, ^{119}Sn MAS NMR, in-situ DRIFTS and XAFS further elucidated the chemical environment and structural role of Sn within the catalyst. Notably, for the XAFS experiments, the samples were pressed into self-supporting pellets and subjected to reduction treatment. After reduction, the reactor valve was closed under H_2 conditions, and the pellets were directly transferred into an Ar-filled glove box, where they were retrieved and hermetically sealed for subsequent XAFS analysis. This procedure effectively avoided air exposure, thereby ensuring the reliability of the subsequent XAFS analysis^[6]. Thus, we believe these techniques collectively mitigate, although not fully substitute, the absence of in-situ XAS data.

Nevertheless, we fully concur with the reviewer that in-situ XAS remains highly desirable. Recognizing this, we have already initiated formal applications for synchrotron beam-time to ensure that future investigations can include such essential

experiments. We commit to prioritizing this characterization in subsequent research to further validate and deepen the understanding of our catalytic systems.

We appreciate the reviewer's constructive suggestion and understanding and believe that the scientific contribution of our current study remains substantial and rigorous, even within the acknowledged experimental constraints.

Reviewer #3 (Remarks to the Author):

Comments 1: *The authors have properly answered my question and I recommend its publishment in "Nature Communication".*

Response: We sincerely appreciate the reviewer's recognition and strong recommendation for publication in Nature Communications. Your valuable comments and suggestions have significantly enhanced the clarity and rigor of our manuscript.

Response References

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- 5 Lefton, N. G. & Bell, A. T. Effects of structure on the activity, selectivity, and stability of Pt-Sn-DeAlBEA for propane dehydrogenation. *ACS Catalysis* **14**, 3986-4000 (2024).
- 6 Liu, N. *et al.* Ensemble effect of the nickel–silica interface promotes the water-gas shift reaction. *ACS Catalysis* **13**, 7347-7357 (2023).

Point-by-Point Responses to the Reviewers' Comments

Reviewer #1 (Remarks to the Author):

Comments 1: *The authors reconstructed a structural model in which 20 Pt atoms are anchored by 5 Sn atoms within an MFI framework containing mesopores. However, I still find this model highly questionable. Firstly, considering that the Sn content per unit cell is only 0.5, how is it possible to locally enrich 5 Sn atoms in such a confined region? What kind of synthesis method could realistically achieve such a high local concentration of Sn? Secondly, the EXAFS data shows an average Pt-Pt coordination number (CN) of 6.7, yet the maximum CN in the authors' 20-atom Pt cluster model is ~ 6. What's the average Pt-Pt coordination number for the 20-atom Pt cluster? Additionally, is the average Pt-O CN in this model consistent with EXAFS data? Furthermore, the 20-atom Pt model was not constructed based on experimental evidence but rather adapted from literature and then fitted to match the experimental results. This approach is fundamentally flawed.*

Response: We sincerely appreciate the reviewer's continued and detailed attention to the theoretical model we proposed. We fully understand the reviewer's concerns regarding the scientific validity of the model construction and its consistency with experimental observations. Here, we would like to respond point-by-point to the reviewer's comments, clarify the scientific rationale behind our research approach, and further explain the necessity and limitations of model construction under the current experimental and theoretical conditions.

Regarding the feasibility of local Sn enrichment. As the reviewer correctly pointed out, the average Sn content per unit cell in the MFI framework is approximately 0.5. However, this value only reflects the large-scale statistical average across the entire sample. In practical catalyst systems, especially under one-pot hydrothermal synthesis conditions, the spatial distribution of doped metal elements (i.e., heteroatoms) often exhibits **significant non-uniformity** [*Nat. Mater.* 2020, 19, 1047–1056; *J. Catal.* 2020, 391, 56–68; *Nat. Catal.* 2023, 6, 254–265]. With the assistance of appropriate structure-directing agents, it is entirely possible for local regions (e.g., mesopore areas) to form environments with relatively enriched heteroatoms [*Nat. Catal.* 2023, 6, 254–265].

Although current experimental techniques still find it challenging to directly observe such local enrichment at the atomic scale, existing literature and experience from

similar systems suggest that the existence of local enrichment cannot be completely ruled out [*Angew. Chem. Int. Ed.* 2023, 62, e202310419]. Therefore, the model we proposed is not intended to describe the overall average structure of the catalyst, but rather to represent a possible local microenvironment constrained by experimental trends, serving to explore its role in the catalytic process.

Regarding the relationship between EXAFS coordination numbers and model coordination numbers. We fully agree with the reviewer that EXAFS data reflect the overall average coordination environment of the system. In our 20-atom Pt cluster model, after DFT optimization, the calculated average Pt-Pt coordination number is 4.8, which is slightly lower than the experimentally fitted value of 6.7. However, even under optimal fitting conditions, EXAFS-derived coordination numbers generally exhibit an uncertainty of 20–30% [Calvin, Scott. XAFS for Everyone. *CRC Press*, 2nd Edition, 2024; *Catal. Today*, 1998, 39, 271–279], meaning that the difference remains within a reasonable tolerance range. Moreover, the Pt–O coordination number of 0.3 in our model matches the experimental fitting result of 0.5. Thus, although the model possesses a certain degree of idealization, its key coordination parameters are consistent with experimental results within acceptable margins, confirming its scientific rationality.

Regarding the source and validity of model construction. We fully understand the reviewer’s rigorous requirement for the model to correspond closely to experimental observations. In fact, given the high degree of atomic-scale heterogeneity in real catalyst systems, even the most advanced techniques, such as aberration-corrected STEM or atom probe tomography (APT), currently face significant challenges in achieving comprehensive and statistically meaningful mapping of Sn and Pt distributions in the MFI framework. Under these limitations, adapting representative structural motifs from the literature and refining them based on experimental data to best match the actual system is a widely adopted and internationally accepted modeling strategy in catalytic mechanism studies [*J. Am. Chem. Soc.* 2022, 144, 15944–15953; *Science*, 2025, DOI: 10.1126/science.adu6907].

In this work, the reconstructed model was not chosen arbitrarily or in isolation, but was systematically built based on experimental observations and literature precedents following scientific reasoning. It is worth noting that both the initially constructed

simple Sn–O–Pt₃ models (based on SiO₂ and MFI supports) and the subsequently refined, more complex Sn–O–Pt₂₀ representative model are capable of reasonably explaining the experimentally observed promotional effect of silanol groups in cooperation with Pt sites in facilitating propane dehydrogenation (PDH) reactions. This indicates that **the proposed mechanism is not model-dependent but intrinsically robust**. Furthermore, the Pt cluster was fully relaxed within the MFI framework during DFT calculations, and the final structure corresponds to the total energy minimum from quantum mechanics but not the initial structure.

Additionally, we independently validated the proposed mechanism through isotope-labeling experiments, using *in-situ* DRIFTS combined with online mass spectrometry monitoring. Both using deuterium-labeled catalysts for propane dehydrogenation and conducting dehydrogenation reactions with deuterated propane on the catalyst surface consistently supported the mechanism that silanol groups cooperate with Pt sites to promote PDH reactions.

In summary. While we acknowledge that the current model cannot comprehensively capture all structural features of the catalyst and retains some degree of idealization, it serves as a scientifically reasonable local representative structure under the current experimental and theoretical constraints. It effectively guides our mechanistic understanding within the range of observable experimental data.

Once again, we sincerely appreciate the reviewer's rigorous review and valuable suggestions, and we are willing to further refine the model design according to the reviewer's specific comment to continuously improve the quality of our work and strive to meet the reviewer's expectations.

The related change is described in the revised manuscript as below.

Recognizing that experimental techniques such as XAFS and STEM provide only ensemble-averaged structural parameters rather than site-specific configurations, our model was not built to reproduce average values, but to represent a plausible local environment constrained by experimental trends. Guided by this rationale, a representative Sn-doped MFI model... Notably, the average coordination numbers of Pt-Pt (4.8) and Pt-O (0.3) in the relaxed structure are reasonably consistent with EXAFS-derived averages, falling within their typical uncertainty ranges (20-30%), which supports the model's structural plausibility.