nature portfolio

Peer Review File

Data-driven Discovery of Pt Single Atom Embedded Germanosilicate MFI Zeolite Catalysts for Propane Dehydrogenation

Corresponding Author: Dr Sicong Ma

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)
This manuscript presented a data-driven catalyst design process for the development of a Pt1@Ge-MFI catalyst. With comprehensive characterizations, including XRD, XPS, HR-TEM, XAFS, and DFT calculations, the authors identified the catalytic active sites as the Pt single atoms embedded within the zeolite framework, stabilized by Ge. This catalyst exhibited great performance for the PDH reaction, with long-term catalytic stability and a propane conversion close to thermodynamic equilibrium and propene selectivity exceeding 98%. Notably, the Pt1@Ge-MFI catalyst was synthesized using a straightforward one-pot approach showing great potential for future application. Given the novelty and the importance of this work, the publication of this manuscript in Nature Communications is recommended. However, a few minor comments are to be addressed before publication.

1. Does the Ge content affect the catalytic performance? Please provide a detailed discussion.

2. The catalyst preparation included hydrothermal crystallization and H2 reduction. It would be interesting to investigate the stability of the Pt1 single sites during the H_2 reduction process? Usually reductive environment leads to Pt nano clusters or particles.

3. Considering the well-known susceptibility of Ge-O bonds to hydrolysis, high temperatures and H_2 atmosphere might induce zeolite framework collapse. Please provide additional data on the stability and behavior of the catalyst under these conditions.

4. It seems that the authors would push the developed catalyst to real industrial application. So, it would be important to test longer TOS (at least 100h for a preliminary evaluation) in Fig. 3a where the conversion was almost above 60%. Although Fig. 3b exhibited excellent stability at different reaction conditions, the conversions were all under 50%, not close to industrial working conditions.

4. Spacing in Fig. 3b ’82 3k’ should be deleted.

5. The grammar and phrasing of the manuscript need to be polished. The author should also double check the present and past tense in the text, and make sure they are consistent.

Reviewer #2

(Remarks to the Author)
In this work, Zhao et al propose a data-driven workflow to identify promising catalysts for the dehydrogenation of propane. The dehydrogenation of propane is a technologically highly important process and finding a rational design strategy to do so would be highly important. I am very supportive of data-driven strategies to identify new, promising materials. The provided manuscript aims to develop such a strategy and presents a material that shows promise along all relevant catalyst metrics, i.e., activity, selectivity, and activity.

While experimental results seem promising, reading through the manuscript left me confused at multiple levels about what has been done and these aspects need to be clarified before I can make any recommendation regarding this manuscript. The most important points are:
- I understand how the geometrical parameters were derived (you just measure them), but it is not clear to me what has been done in terms of energetic descriptors.
- In principle, each zeolite structure has multiple exchange positions for Ge atoms. How is it then possible that each zeolite structure only shows up with only one energy value? E.g., MFI has 12 symmetrically distinct T sites. Has Ge been inserted in each one of them and only the most stable value is reported?
- How has Pt been inserted to assess its stability? Is it in an extra framework position, is it inserting into a Ge-O bond? Did the authors only rely on the MD approach described to find the most stable position? Have multiple Ge positions been considered for each zeolite framework?
- What was the strategy to choose the various energetic thresholds? I did not find any reasoning or citations in the paper. This needs to be clarified!
- To me it seems that the largest achievement by the authors was that they found a material that stabilizes small Pt particles under reaction conditions. As was shown by the authors, metal particles form during calcination. At the same time the authors screened for stable small Pt structures. What energies are reported? Is it just DFT energies and these values serve as proxy for stability under reaction conditions? Why would that work?
- It is always encouraging to find materials that show great performance. However, a screening strategy should always be evaluated by its success rate, not only for finding one specific system that works. Have the authors tested the performance of another zeolite that is predicted to be ideal for this reaction? As far as I understand, the Ge form of IWW is relatively straightforward to synthesize and - if the screening approach of the authors is viable - should also show great performance. Have the authors tested the performance of Pt-Ge-IWW?
- I believe the term AI-based atomic simulation is a reach. This implies that some type of automated approach has been developed to perform electronic structure calculations. This is not the case. I encourage the authors to clarify this aspect throughout the manuscript.
- There are several points of good scientific practice and data-transparency that are missing in this manuscript:
- The authors indicate that they used their ML-based force fields to identify promising structures and then perform DFT calculations for the most stable structures. It would be good to show the energies for different structures that the reader can assess whether the choices made are reasonable. This is particularly important, since the error of their approach is ~0.5 eV per structure of this admittedly large unit cell.
- I believe it is important to include the structural files of at least the various structures shown in the manuscript, but ideally of all the energetic datapoints provided in the SI database. This way, other researchers can confirm whether the optimized structures are reasonable or not.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
After carefully re-evaluating the manuscript, I find that the authors have adequately addressed my concerns. I recommend the paper for prompt publication. However, I have noticed a few minor grammatical errors that should be corrected before final acceptance:
1. In the last sentence of the abstract, "holds the promise for" should be revised to "holds promise for", and "be rooted from" should be corrected to "be rooted in" for grammatical accuracy.
2. The word "nearby" has been used multiple times in the manuscript, where "near" would be more appropriate.
I encourage the authors to make these minor revisions to ensure clarity and correctness in the final version.

Reviewer #2

(Remarks to the Author)
First, I want to thank the authors for the work they have done with the recent revisions. Many of the points considering the scientific validity I brought up have been successfully resolved. At this stage, I only have some comments concerning the wording in a few spots of the manuscript:
- In the abstract the authors state "We showed
that out of the zeolite database (>220 structure framework)
and more than 100,000 Pt/Ge differently distributed configu-
rations, there were only three Ge-containing zeolites, ger-
manosilicate (MFI, IWW and SAO) that were capable to stabi-
lize Pt single atom embedded in zeolite skeleton and at the
meantime allowed propane fast diffusion." This statement is not true. The authors screened materials and identified three promising candidate materials. The current wording implies that the authors tested all these materials experimentally. This should be corrected. (E.g. Our screening study of XXX identified three germanosilicate materials, that ....)
- I suggest similar changes on page 2 (left column) for the sentence "from which only three germanosili-
cate zeolites (MFI, IWW and SAO) were identified that were ca-
pable of stabilizing Pt single atoms in zeolite skeleton with the
help of Ge and at the meantime allowed fast propane diffusion."

- I believe that the paragraph " When incorporating the Ge element into the zeolite framework, we could design a replacement energy metric (ΔErep) to quantify the energy change arising from the substitution of one Si atom in the pure silica zeolite framework by Ge(OH)4, resulting in the formation of germanosilicate zeolite and Si(OH)4, as illustrated in Eq. 1. Based on the structure of more than thirty synthesized SiGe zeolites known in experiments, we determined that a threshold of 0.35 eV for ΔErep as a thermodynamics descriptor to screen the feasibility of Ge replacement in experiment, where 90% of experimentally synthesized SiGe zeolites have ΔErep values less than 0.35 eV (also see Figure S1 and Table S1)." needs a couple of clarifications:
- It should specifically mention that Ge is in its most stable T site.
- I like figure S1. It could be very valuable for many people in the field! However, I am not sure where the data in Figure S1 comes from. Was literature data used to construct this plot? If so, the different datapoints should be referenced and an exclusive list of citations should be added. It is only fair to the people who did this work.
- Page 7, left column: The authors state: "Our results were distinct from the traditional picture that the active sites for PDH reaction were small Pt clusters. " I believe that the authors managed to stabilize single Pt atoms. However, I also believe that other groups stabilized Pt particles in zeolites. It should be clarified in the discussion below that there are clear differences between the different materials presented in this work and other literature studies. I believe this is one of the main achievements of this work and should be correctly put in the context of the scientific literature. As of now, the given discussion section fails to do that. To put it differently: The authors provide the necessary information, but it is not arranged in an effective way. If they manage to do that, this manuscript will be significantly improved.
- Page 7, right column: " To recap, this work proposed an AI-driven catalyst design strategy to search stable metal@zeolite catalysts for PDH reaction."
I do nto believe that the wording: AI-driven catalyst design is appropriate, since AI was only used to identify starting structures for DFT calculations. A more accurate wording would be: 'In this work we used a screening based approach to identify stable metal@zeolite catalysts for the PDH reaction.'

Revision report (response to the referees' specific comments)

Referee 1

Comment (1): Does the Ge content affect the catalytic performance? Please provide a detailed discussion.

Reply: Thank you for pointing it out. We have added corresponding points in the Supplementary Information (quoted below).

"To clarify the effect of Ge content on the catalytic performance, we synthesized a series of samples with different Ge content, as detailed in the Si:Ge ratios and catalytic performance shown in the figure below.

The comparison of catalytic performance between Pt@MFI and Pt@Ge-MFI-222 highlights that a small amount of Ge enhances propane conversion and stability. However, this improvement remains suboptimal. As the Si:Ge ratio decreased to 140, the stability improved, though some deactivation was still evident. Notably, when the Si:Ge ratio was reduced further to 64 and 37, the PDH reaction reached and maintained equilibrium conversion. This suggests that, under a WHSV of 1.75, the Ge content in Pt@Ge-MFI-64 was sufficient for effectively anchoring Pt."

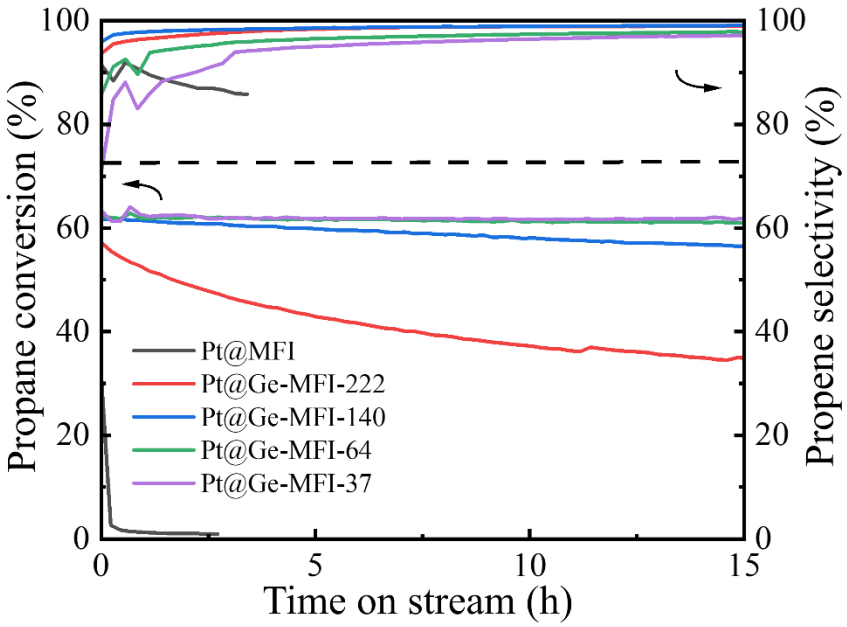

Figure R1. The catalytic performance of Pt@Ge-MFI catalysts with various Si:Ge ratios, which are indicated as suffixes in the sample names. The catalysts were pre-treated in H_2 flow for 4 hours, and the PDH reaction was carried out under the condition of $WHSV_{propane}$ = 1.75h^{-1}, propane/N_2 = 1/3, 873 K and atmospheric pressure.

Comment (2): The catalyst preparation included hydrothermal crystallization and H_2 reduction. It would be interesting to investigate the stability of the Pt_1 single sites during the H_2 reduction process? Usually reductive environment leads to Pt nano clusters or particles.

Reply: The structural evolution of Pt species under reducing conditions was probed

through in-situ XRD with programmed thermal treatment in H_2. The experiment protocol comprised three phases: (i) Baseline acquisition at 303 K, (ii) temperature-programmed analysis with 2 K/min ramp rate and isothermal holds during data collection, and (iii) an extended 4-hour dwell at 873 K simulating industrial pre-reduction.

As evidenced in Figure R2, the characteristic Pt(111) reflection at 39.76 ° remained conspicuously absent throughout the reduction protocol, including after prolonged high-temperature exposure. This suppression of Pt nanoparticle coalescence was independently verified by atomic-resolution TEM (Figure 2c,d), which revealed exclusively subnanometric Pt clusters. The collective data confirm the exceptional thermal stability of Pt@Ge-MFI's anchored Pt species in H_2. As detailed in Figure S9, air calcination at 773 K induced pronounced Pt(111) diffraction (centered at 39.76 °), corresponding to nanometric metallic Pt particles.

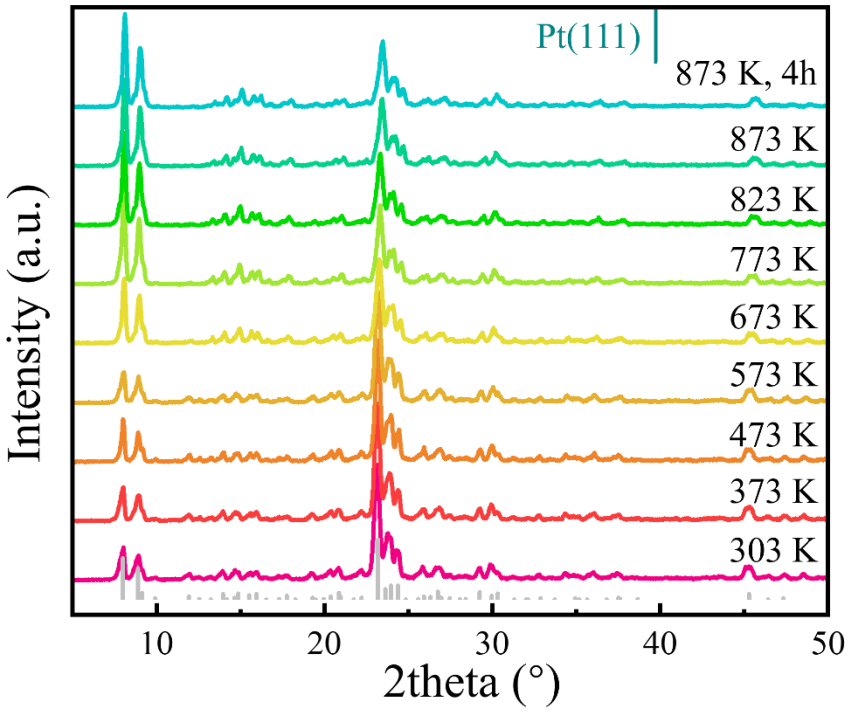

Figure R2. In-situ XRD patterns of Pt@Ge-MFI(r) during H_2 reduction under increasing temperatures, where r refers to the raw sample without H_2 pre-reduction or air calcination. The grey pattern is the standard pattern of Mutinaite (PDF#44-0002), an MFI-type mineral.

Comment (3): Considering the well-known susceptibility of Ge-O bonds to hydrolysis, high temperatures and H_2 atmosphere might induce zeolite framework collapse. Please provide additional data on the stability and behavior of the catalyst under these conditions.

Reply: To systematically investigate structural stability under harsh conditions, we

conducted in situ XRD characterization under flowing H_2 at 873 K (Figure R2). Remarkably, the diffraction patterns collected following 4-hour exposure at 873 K retained identical peak positions compared to both the initial high-temperature measurement and the room-temperature baseline (303 K), demonstrating exceptional preservation of the germanosilicate zeolite framework under reductive thermal stress. To provide complementary structural validation, comparative XRD analyses of three catalyst variants—Pt@Ge-MFI(r), Pt@Ge-MFI, and Pt@Ge-MFI(s)—were performed under ambient conditions. The nearly superimposable patterns (Figure R3), exhibiting matching peak positions and intensities across all samples, further corroborate the architectural robustness of the catalyst system. This combined evidence conclusively demonstrates the material's dual stability: thermal resilience under prolonged H_2 exposure and structural integrity maintenance during reactive operation.

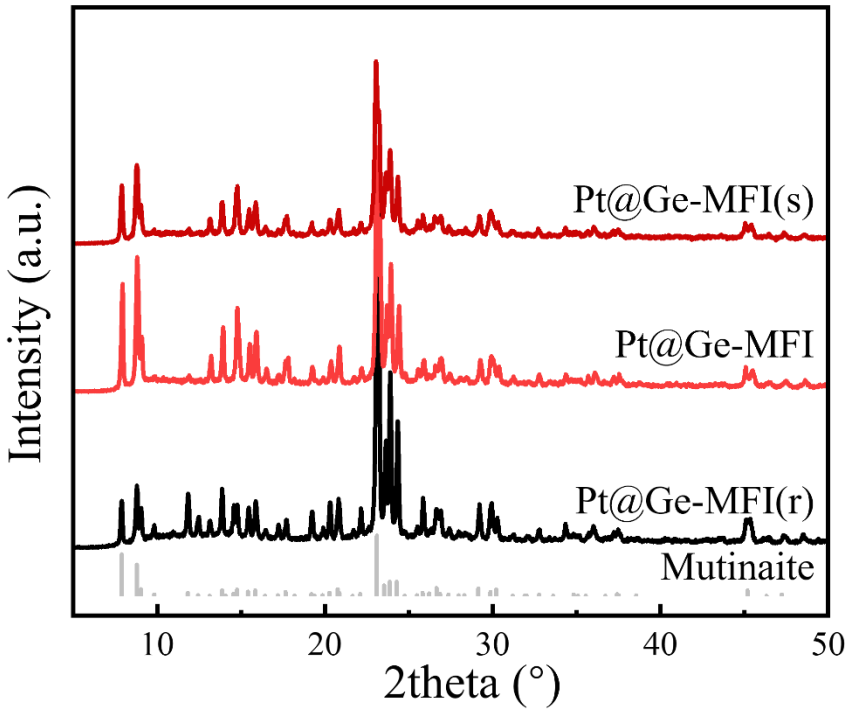

Figure R3. XRD patterns of Pt@Ge-MFI(r), Pt@Ge-MFI, Pt@Ge-MFI(s), and standard pattern of Mutinaite (PDF#44-0002), where r refers to the raw sample without H_2 pre-reduction and s refers to the spent sample obtained after 12 hours' PDH reaction at 873 K.

Comment (4): It seems that the authors would push the developed catalyst to real industrial application. So, it would be important to test longer TOS (at least 100h for a preliminary evaluation) in Fig. 3a where the conversion was almost above 60%. Although Fig. 3b exhibited excellent stability at different reaction conditions, the conversions were all under 50%, not close to industrial working conditions.

Reply: As shown in Figure R4, we conducted a 120-hour stability test under the same

conditions as in Figure 3a (WHSVpropane = 1.75 h^{-1}, propane/N_2 = 1/3, 873 K, and atmospheric pressure). During the initial stages of the reaction, the propylene selectivity rapidly increased to 95%, and it further improved to over 98% as the reaction progressed. Meanwhile, propane conversion remained stable above 60% throughout the test. These results demonstrate that the catalyst not only maintains long-term stability but also delivers exceptional selectivity under harsh conditions.

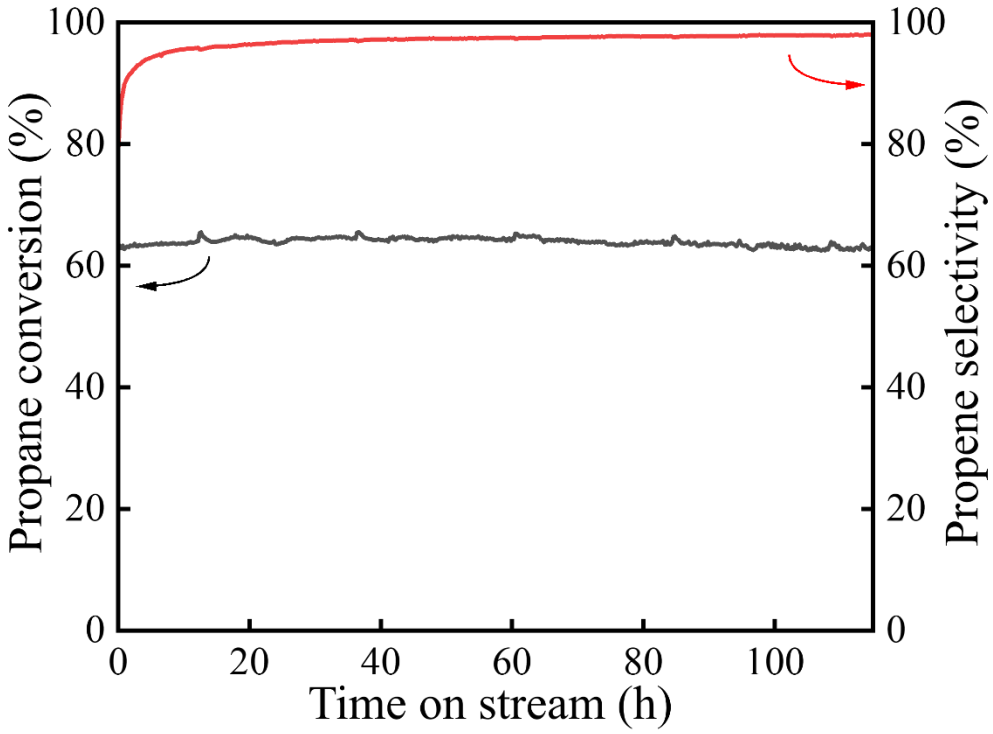

Figure R4. The catalytic performance of Pt@Ge-MFI under the condition of $WHSV_{propane}$ = 1.75 h^{-1}, propane/N_2 = 1/3, 873 K and atmospheric pressure.

Comment (5): Spacing in Fig. 3b '82 3k' should be deleted.
Reply: We have reviewed Figure 3b and corrected the formatting issue.

Comment (6): The grammar and phrasing of the manuscript need to be polished. The author should also double check the present and past tense in the text, and make sure they are consistent.
Reply: Thanks, we have revised the tense in manuscript.

Referee 2
Comment (1): I understand how the geometrical parameters were derived (you just measure them), but it is not clear to me what has been done in terms of energetic descriptors.
Reply: Thank you for your thoughtful comment. We would like to clarify the steps we took in defining and calculating the energy descriptors, which were introduced

primarily from the perspective of catalyst synthesis.

The first energy descriptor ensures that the zeolite framework is stable with pure SiO_2 components. Zeolites are often synthesized with additional components like SiAl or SAPO. The introduction of elements such as Al or P can induce acidity, which is undesirable for the propane dehydrogenation (PDH) reaction. Therefore, it is crucial to ensure that the zeolite framework consists of pure SiO_2 for effective catalyst synthesis. Our previous work demonstrated that zeolites with cages must have an energy lower than the double-layer (DL) phase but higher than the densely packed quartz phase. [1, 2] For SiO_2 zeolites, the presence of the SiO_2 DL phase (0.18 eV per formula unit above quartz) sets the upper energy bound, as shown in Figure R5.

The second descriptor focuses on the incorporation of Ge into the zeolite framework. To quantify the potential for Ge substitution, we introduced the replacement energy metric ($\boldsymbol{\Delta E_{rep}}$), which calculates the energy change when a Si atom is replaced by a Ge atom in the framework. During the hydrothermal process, Ge and Si primarily exist as $Ge(OH)_4$ and $Si(OH)_4$, which we used as reference states for the replacement energy calculation, as shown in Eq. 1. Based on experimental studies involving more than thirty SiGe zeolites, we found that a $\boldsymbol{\Delta E_{rep}}$ value of 0.35 eV serves as a reliable threshold, as shown in Figure R6. This value accurately predicts the feasibility of Ge incorporation, as over 90% of synthesized SiGe zeolites have $\boldsymbol{\Delta E_{rep1}}$ values below this threshold.

$$\boldsymbol{\Delta E_{rep}}: \quad Zeo[SiO_2] + Ge(OH)_4 \rightarrow Zeo[GeSiO_2] + Si(OH)_4 \qquad (1)$$

The third descriptor ensures that the Ge element can stabilize Pt atoms, which can exist either as single atoms (Pt_1) or clusters (e.g., Pt_4). We assessed the stabilizing effect of Ge on both forms by calculating the corresponding energy changes for Pt single atoms ($\boldsymbol{\Delta E_{Pt1}}$) and Pt clusters ($\boldsymbol{\Delta E_{Pt4}}$) using Eq. 2 and Eq. 3, respectively. If either $\boldsymbol{\Delta E_{Pt1}}$ or $\boldsymbol{\Delta E_{Pt4}}$ is below 0, it indicates that Ge can stabilize Pt. Based on these calculations, we determined that zeolites in regions II, III, and IV meet the requirement for stabilizing Pt, as shown in Figure R7. However, if the goal is to stabilize Pt single atoms rather than Pt clusters, we recommend focusing on region II, as only in this region does Ge stabilize Pt single atoms without stabilizing Pt clusters. As a result, we identify only three zeolites (MFI, IWW, and SAO) that satisfy all the criteria. This discussion has been added to the revised manuscript for improved clarity.

$$\boldsymbol{\Delta E_{Pt1}}: \quad Pt_1@SiO_2 + Zeo[GeSi] \rightarrow Pt_1@Ge\text{-}SiO2 + Zeo[SiO_2] \qquad (2)$$

$$\boldsymbol{\Delta E_{Pt4}}: \quad Pt_4@ SiO_2 + Zeo[GeSi] \rightarrow Pt_4@Ge\text{-}SiO_2 + Zeo[SiO_2] \qquad (3)$$

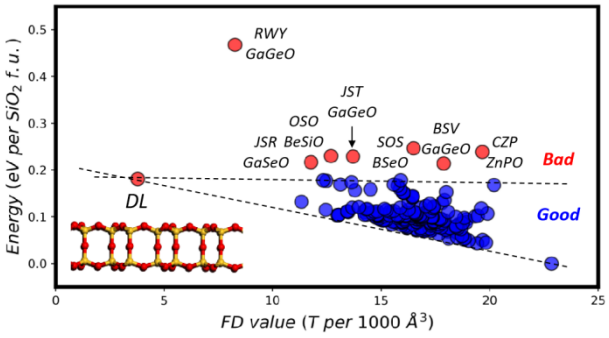

Figure R5. The energy variations against framework density (FD) value for SiO_2 with

252 as-synthesized zeolite frameworks, where the double layer (DL) phase with the energy of 0.18 eV per SiO_2 formula unit (f.u.) relative to the quartz phase can be utilized as a convenient measure to judge whether a proposed zeolite framework is likely to be synthesized or not.

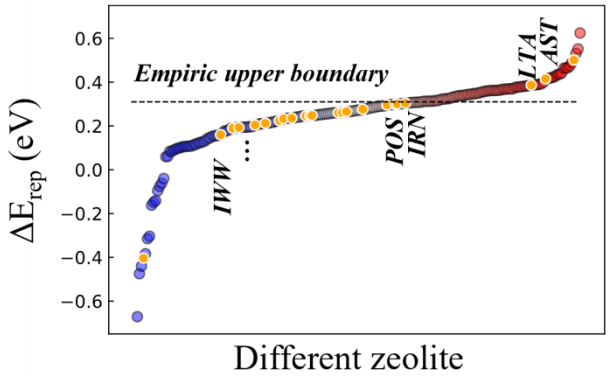

Figure R6. The variation of replacement energy of Si by Ge for different zeolite skeletons.

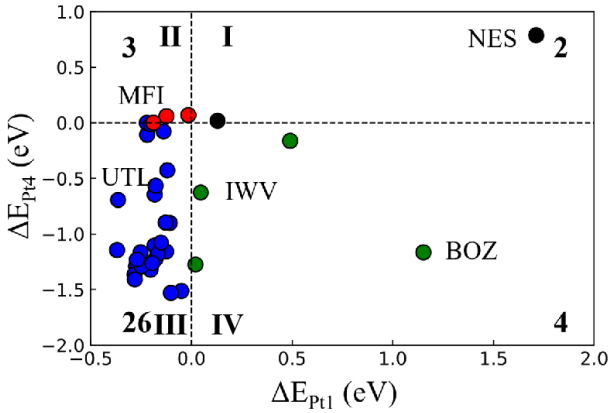

Figure R7. The relative stability energy of different Pt existent forms in Ge-doping zeolite compared to the pure silica zeolites, where the x and y axes represent the Pt existence forms of Pt single atom in zeolite skeleton and the Pt_4 cluster in zeolite channel, respectively.

Comment (2): In principle, each zeolite structure has multiple exchange positions for Ge atoms. How is it then possible that each zeolite structure only shows up with only one energy value? E.g., MFI has 12 symmetrically distinct T sites. Has Ge been inserted in each one of them and only the most stable value is reported?

Reply: Yes, we have calculated all possible T sites for Ge substitution, but only the most stable site is reported for each zeolite structure. This is why each zeolite structure is associated with a single energy value in our results. The detailed calculation process has been included in the Method section for further clarity.

Comment (3): How has Pt been inserted to assess its stability? Is it in an extra framework position, is it inserting into a Ge-O bond? Did the authors only rely on the MD approach described to find the most stable position? Have multiple Ge positions

been considered for each zeolite framework?

Reply: We appreciate your interest in the details of the Pt insertion and stability assessment process. Allow us to clarify the methodology used for incorporating Pt and Ge into the zeolite frameworks.

First, we identified the most stable position for Ge within the zeolite framework, as explained in the previous section. Once the Ge position was determined, we replaced the Si atoms in the zeolite skeleton with Pt and explored all possible positions for Pt substitution. This approach enabled us to calculate the energetics of each potential Pt-Si replacement, ultimately revealing the most stable position for the Pt single atom.

For the Pt_4 cluster, after establishing the Ge position, we introduced the Pt_4 cluster into the zeolite channel near the Ge site. To optimize the position of the Pt_4 cluster, we performed Stochastic Surface Walking with Neural Networks (SSW-NN) simulations, allowing for a more efficient exploration of the potential energy surface. Over 2000 minima were examined for each zeolite framework to identify the most stable configuration of the Pt_4 cluster.

This comprehensive approach ensured that the most stable Pt_4 configuration in the presence of Ge was accurately determined. The detailed calculation process has been included in the Method section and is also provided below for further clarity.

"*With the G-NN potential, we were able to efficiently explore the PES of Pt-Ge-Si-O-H systems. For each zeolite skeleton, we enumerated and calculated all possible T sites for Ge substitution, from which the most stable position for Ge within the framework was identified. We then replaced the Si atoms nearby the Ge atom by Pt and investigated the possible substitution sites for a single Pt atom. This allowed us to determine the best Pt-O-Ge configuration (Pt_1) in the zeolite framework. For the configuration of Pt_4 cluster, we introduced the Pt_4 cluster into the zeolite channel near the Ge position and explored the structure configurations using SSW-NN. Over 2000 minima were examined for each zeolite framework to determine the most stable configuration of the Pt_4 cluster, which ensured the finding of the most stable Pt_4 configuration in the presence of Ge. Finally, all the low energy structure candidates from G-NN potential calculations were finally verified by plane wave DFT calculations and thus the energetic data reported in the work, without specifically mentioning, was from DFT.*"

Comment (4): What was the strategy to choose the various energetic thresholds? I did not find any reasoning or citations in the paper. This needs to be clarified!

Reply: Thank you for your comment and for highlighting the need for clarification regarding the choice of energetic thresholds. As mentioned in **Comment (1)**, the reasoning behind the selection of energetic thresholds has already been discussed in detail. Also, we have clarified these points in the Results and discussion section, which are presented below as well.

"Our previous work proved that zeolites with cage structures are in general more stable than a double layer (DL) SiO_2 phase, but less stable than the densely packed quartz phase. The SiO_2 DL phase, being 0.18 eV per f.u. above quartz, thus dictates the upper energy bound of any SiO_2 zeolite structure serving as a practical benchmark for

assessing the stability of pure silica composition."

"Based on the structure of more than thirty synthesized SiGe zeolites known in experiments, we determined that a threshold of 0.35 eV for ΔErep as a thermodynamics descriptor to screen the feasibility of Ge replacement in experiment, where 90% of experimentally synthesized SiGe zeolites have ΔE_{rep} *values less than 0.35 eV (also see Figure S1 and Table S1)."*

"Fourth, the Ge element must provide extra stabilization to Pt. Considering that Pt after reduction could exist as either single atoms (Pt_1*) or small clusters (e.g.* Pt_4*), we measured the stabilizing effect of Ge on Pt in both forms. The relative stability energy metrics,* ΔE_{Pt1} *and* ΔE_{Pt4}*, are utilized to assess the energy change of the Pt single atom and Pt cluster moving close to the Ge site in the zeolite framework, respectively, as shown in Eq. 2-3. Obviously, the negative* ΔE_{Pt1} *or* ΔE_{Pt4} *is desirable, indicating that Ge can stabilize Pt. To prevent Pt segregation, our goal is to maximally stabilize Pt single atoms, not Pt clusters, and thus we will screen germanosilicate zeolites with negative* ΔE_{Pt1} *(*$\Delta E_{Pt1} < 0$*) but positive* ΔE_{Pt4} *(*$\Delta E_{Pt4} > 0$*) (also see Figure S2 and Table S1)."*

Comment (5): To me it seems that the largest achievement by the authors was that they found a material that stabilizes small Pt particles under reaction conditions. As was shown by the authors, metal particles form during calcination. At the same time the authors screened for stable small Pt structures. What energies are reported? Is it just DFT energies and these values serve as proxy for stability under reaction conditions? Why would that work?

Reply: During the screening process, our goal was to identify zeolite frameworks capable of stabilizing Pt. To achieve this, we used a unified Pt coordination model (e.g., Pt single atoms coordinated to four O atoms and connected to Ge via oxygen bridges, i.e., [$GeOPtO_3$]). DFT calculations were performed to assess the effect of the zeolite skeleton on Pt stability. Although the DFT calculations were conducted at 0 K, the model used effectively represents an O-rich situation, which is relevant for the conditions typically encountered in zeolite synthesis. Once the zeolite screening was completed, our focus shifted to identifying the real catalytic active sites under actual reaction conditions. At this point, the model must be adjusted to reflect the changes that occur under PDH reaction conditions. For instance, Pt single atoms with the [$GeOPtO_3$] configuration are no longer stable under reaction conditions and tend to undergo reduction by H_2, forming the [$GePtO_3H_2$] configuration. To assess whether this transformation is thermodynamically favorable, we performed Gibbs free energy corrections, which allowed us to identify the actual catalytic active sites under realistic conditions. Therefore, the zeolite synthesis typically occurs under O-rich conditions, and our [PtO_4] model serves as a good representation of Pt species under those conditions. This is why the DFT calculations at 0 K are effective for the initial screening, as they correctly capture the stable Pt species in the context of the O-rich environment.

Comment (6): It is always encouraging to find materials that show great performance. However, a screening strategy should always be evaluated by its success rate, not only for finding one specific system that works. Have the authors tested the performance

of another zeolite that is predicted to be ideal for this reaction? As far as I understand, the Ge form of IWW is relatively straightforward to synthesize and - if the screening approach of the authors is viable - should also show great performance. Have the authors tested the performance of Pt-Ge-IWW?

Reply: We sincerely appreciate the reviewer's insightful suggestion regarding the importance of evaluating the performance of our screening strategy across multiple zeolite frameworks. We have previously made several attempts to synthesize Pt@Ge-IWW and Ge-IWW materials following the methodology reported by Lu et al. While Ge-IWW was successfully synthesized, all attempts to prepare Pt@Ge-IWW proved unsuccessful. These results have been documented in the Results and discussion section (quoted below for clarity).

"Among three zeolites, SAO zeolite is difficult to synthesize: a recent synthesis of SAO zeolite, involving a non-commercial N,N'-diethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidine as OSDA, suggests a prohibitive cost to industrialization. Similarly, the synthesis of IWW zeolite also requires a large OSDA molecule, e.g. 1,4-bis-(dimethyl-1-adamantylammonium)-butane. Our preliminary synthetic tests indicated that it is not straightforward to encapsulate Pt into IWW zeolite because ethylenediamine (EDA) molecules commonly utilized to protect Pt source interfere the zeolite crystallization, leading to poorly crystalized material other than IWW zeolite (see Figure S3). By contrast, the synthesis of MFI zeolite with a large volume of experimental literatures is facile and has a low cost. Furthermore, the EDA introduced with Pt source can even act as the OSDA of MFI zeolite. We thus select MFI as candidate for further catalysis experiments."

Also, we have now included the detailed Pt@Ge-IWW synthesis protocol and corresponding XRD patterns in Supplementary Information (quoted below).

*"**Synthesis of Ge-IWW zeolites:** The OSDA utilized for IWW was 1,4-bis-(dimethyl-1-adamantylammonium)-butane, whose synthesis were reported by Lu K. et al. The synthesis gel had an overall molar ratio of Si: Ge: OSDA: H_2O = 1: 0.5 : 0.3 : 20. The gel was stirred for 3 hours (500 rpm) at ambient temperature before transferred to a 50 mL Teflon-lined autoclave. Afterwards, the hydrothermal synthesis was carried out at 175 °C for 72 hours in an electric oven. The product was washed and dried at 80 °C. The XRD patterns were collected subsequently for analysis.*

***Synthesis of Pt@Ge-IWW zeolites:** The trial for Pt@Ge-IWW synthesis followed the same protocol as that for Ge-IWW, except that Pt precursor solution was added to the synthesis gel before stirring and hydrothermal synthesis. However, the XRD pattern of the resulting product could not match any known zeolites."*

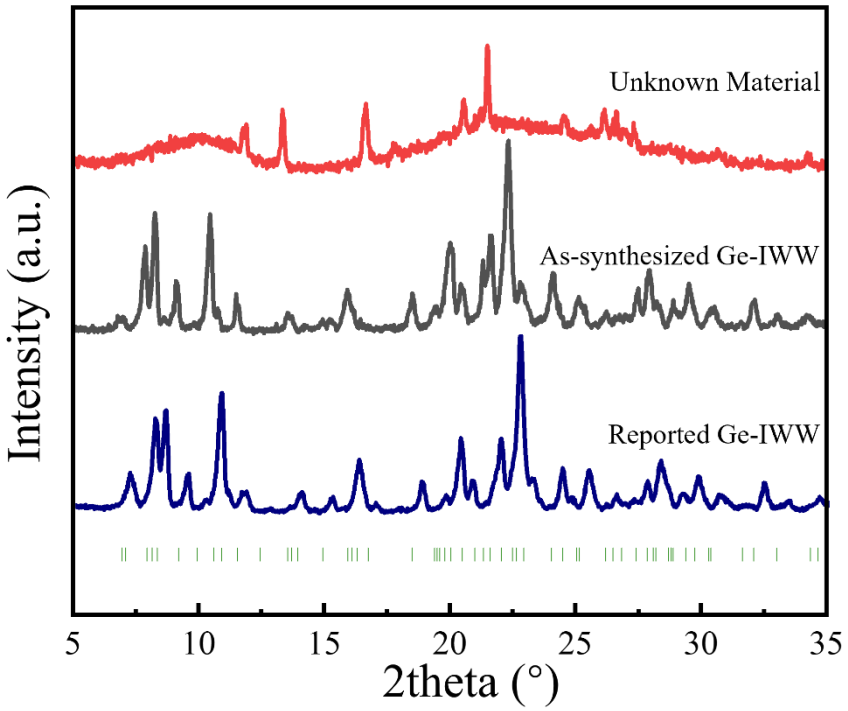

Figure R8. XRD patterns of the unknown material obtained from the trial synthesis of Pt@Ge-IWW, as-synthesized Ge-IWW and reported Ge-IWW by Lu et al.,[3] where the green lines are the calculated peaks of IWW zeolite.

Comment (7): I believe the term AI-based atomic simulation is a reach. This implies that some type of automated approach has been developed to perform electronic structure calculations. This is not the case. I encourage the authors to clarify this aspect throughout the manuscript.

Reply: We have revised the terminology in the manuscript and replaced "AI-based atomic simulation" with "G-NN-based atomic simulation" (Global Neural Network). This change ensures that the description more accurately reflects the methodology used in our study.

Comment (8): There are several points of good scientific practice and data-transparency that are missing in this manuscript:

- The authors indicate that they used their ML-based force fields to identify promising structures and then perform DFT calculations for the most stable structures. It would be good to show the energies for different structures that the reader can assess whether the choices made are reasonable. This is particularly important, since the error of their approach is ~0.5 eV per structure of this admittedly large unit cell.
- I believe it is important to include the structural files of at least the various structures shown in the manuscript, but ideally of all the energetic data points provided in the SI database. This way, other researchers can confirm whether the optimized structures

are reasonable or not.

Reply: Thanks for your valuable comments. We have added the energy and structure information in the Supporting Information. Additionally, to make these structures more accessible, we have uploaded them to our own database and made them available through a webpage where the germanosilicate zeolite with the most stable configuration for each zeolite skeleton after DFT optimization are shown (www.lasphub.com/database/#/zeodopedGe). This will allow others to verify the optimized structures and assess their reasonableness.

References

1. Ma S, Liu Z-P. Machine learning potential era of zeolite simulation. *Chemical Science* 2022, **13**(18)**:** 5055-5068.

2. Ma S, Shang C, Wang C-M, Liu Z-P. Thermodynamic rules for zeolite formation from machine learning based global optimization. *Chemical Science* 2020, **11**(37)**:** 10113-10118.

3. Lu K, Huang J, Jiao MC, Zhao YH, Ma Y, Jiang JG*, et al.* Topotactic conversion of Ge-rich IWW zeolite into IPC-18 under mild condition. *Microporous and Mesoporous Materials* 2021, **310**.

Question:	Reply:
In the last sentence of the abstract, "holds the promise for" should be revised to "holds promise for", and "be rooted from" should be corrected to "be rooted in" for grammatical accuracy.	The phrase has been revised to “holds promise for” and “be rooted in”.
The word "nearby" has been used multiple times in the manuscript, where "near" would be more appropriate.	The instances of “nearby” have been uniformly replaced with “near” throughout the manuscript.
In the abstract the authors state "We showed that out of the zeolite database (>220 structure framework) and more than 100,000 Pt/Ge differently distributed configurations, there were only three Ge-containing zeolites, germanosilicate (MFI, IWW and SAO) that were capable to stabilize Pt single atom embedded in zeolite skeleton and at the meantime allowed propane fast diffusion." This statement is not true. The authors screened materials and identified three promising candidate materials. The current wording implies that the authors tested all these materials experimentally. This should be corrected. (E.g. Our screening study of XXX identified three germanosilicate materials, that ....)	The sentences in the abstract are revised as detailed below. *“We show that out of the zeolite database (>220 structure framework) and more than 100,000 Pt/Ge differently distributed configurations, there are only three Ge-containing zeolites, germanosilicate (MFI, IWW and SAO) that are predicted to be capable of stabilizing Pt single atom embedded in zeolite skeleton and at the meantime allowing propane fast diffusion. Among, the Pt_1@Ge-MFI catalyst is successfully synthesized via a simple one-pot synthesis…”*
I suggest similar changes on page 2 (left column) for the sentence "from which only three germanosilicate zeolites (MFI, IWW and SAO) were identified that were capable of stabilizing Pt single atoms in zeolite skeleton with the help of Ge and at the meantime allowed fast propane diffusion."	Similarly, we make some complementary statement after the sentence, as detailed below. *“This designed catalyst was synthesized via a simple one-pot synthetic approach without any post-treatment in MFI framework.”*
I believe that the paragraph " When incorporating the Ge element into the zeolite framework, we could design a replacement energy metric (ΔE_{rep}) to quantify the energy change arising from the substitution of one Si atom in the pure silica zeolite framework by Ge(OH)4, resulting in the formation of germanosilicate zeolite and Si(OH)4, as illustrated in Eq. 1. Based on the structure of more than thirty synthesized SiGe zeolites known in experiments, we determined that a	Supplementary discussion on the most stable T site is appended as below. *“When incorporating the Ge element into the zeolite framework, we could design a replacement energy metric (ΔE_{rep}) to quantify the energy change arising from the substitution of one Si atom in the pure silica zeolite framework by $Ge(OH)_4$, resulting in the formation of germanosilicate zeolite and $Si(OH)_4$, as illustrated in Eq. 1, where all germanosilicate zeolite structures are the most*

threshold of 0.35 eV for ΔE_{rep} as a thermodynamics descriptor to screen the feasibility of Ge re- placement in experiment, where 90% of experimentally synthesized SiGe zeolites have ΔE_{rep} values less than 0.35 eV (also see Figure S1 and Table S1)." needs a couple of clarifications: It should specifically mention that Ge is in its most stable T site.	*stable structures by exploring all possibilities of the substitution of Si by Ge."*
I like figure S1. It could be very valuable for many people in the field! However, I am not sure where the data in Figure S1 comes from. Was literature data used to construct this plot? If so, the different datapoints should be referenced and an exclusive list of citations should be added. It is only fair to the people who did this work.	The data in Figure S1 is the ΔE_{rep} values of all germanosilicate zeolites, where the data is calculated by us and can be found in Table S1 and the online website of www.lasphub.com/database/#/zeodopedGe.
Page 7, left column: The authors state: "Our results were distinct from the traditional picture that the active sites for PDH reaction were small Pt clusters. " I believe that the authors managed to stabilize single Pt atoms. However, I also believe that other groups stabilized Pt particles in zeolites. It should be clarified in the discussion below that there are clear differences between the different materials presented in this work and other literature studies. I believe this is one of the main achievements of this work and should be correctly put in the context of the scientific literature. As of now, the given discussion section fails to do that. To put it differently: The authors provide the necessary information, but it is not arranged in an effective way. If they manage to do that, this manuscript will be significantly improved.	We have revised the description and focused on the differences of our results with literature about the Pt existence form, i.e. Pt cluster or Pt single atom. The revised the manuscript are copied below. *"Lots of previous literature proves that the active sites for PDH reaction were small Pt clusters.[47-52] Along the guidance, many strategies were proposed to mitigate the strong thermodynamic tendency of Pt cluster growth and thus keep the fine Pt dispersion, e.g. via strong metal-support interactions, Sn alloying, support amorphorization, and zeolite confinement.[27] The zeolite confinement approach might be further benefited by the addition of second elements (such as Sn,[53,54] Ga,[55,56] In,[57,58] and Zn[59-61]) to stabilize Pt clusters by modifying the electronic structure of Pt or providing the anchoring sites, although not all elements (e.g. Al[57,62]) were effective. While, our results of Pt@Ge-MFI proved that Pt single atom site in zeolite could also exhibit the excellent PDH catalytic performance and thus provided a new, atom-economic solution to anchor and disperse single Pt in zeolite."*

Page 7, right column: " To recap, this work proposed an AI-driven catalyst design strategy to search stable metal@zeolite catalysts for PDH reaction." I do not believe that the wording: AI-driven catalyst design is appropriate, since AI was only used to identify starting structures for DFT calculations. A more accurate wording would be: 'In this work we used a screening-based approach to identify stable metal@zeolite catalysts for the PDH reaction.'	We have changed the word “AI-driven” into “data-driven”. We maintain that “data-driven” accurately reflects the methodological foundation of our work.