nature portfolio

Peer Review File

Continuous photo-oxidation of methane to methanol at an atomically tailored reticular gas-solid interface

Corresponding Author: Professor Jinhua Ye

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 paper reported a metal-organic framework (MOF) membrane nanoreactor, by introducing Pd and Fe on the MOF node as POR and HMO sites, achieving high photocatalytic tandem methane oxidation (PTMO) performance at the gas-solid interface. Some results are very interesting and would promote the development of this field. Some revisions are still required before final acceptance, as detailed in the following comments.

1. Page 6 line 136-148: The author grafted Pd species onto the Zr–O nodes as POR sites to form the Pd1/aUiO catalyst, provided the H2O2 yield corresponding to the catalysts with different Pd loadings in Supplementary Fig. 12, and noted the difference between Pd1/aUiO (0.78) and Pd1/aUiO (0.83) in the manuscript. Please explain the reason for increasing the Pd loading to 0.83 wt.% and why not choose a higher loading of Pd (such as 1 wt.%) for the comparison. The author claimed that “This suggests there were no sufficient bonding sites on Zr–O nodes for additionally anchoring atomically dispersed metal species.” Please use the mass of Pd instead of the mass of the catalyst to calculate the yield of H2O2 and discuss the relationship between H2O2 yield and Pd species.

2. Page 8 line 174-178: The author showed that the catalyst treated with dilute sulfuric acid showed significant changes in the surface area and pore volume. Please provide the surface area and pore volume results of the Pd1/aUiO(H), to indicate that this phenomenon is caused by the leaching of iron oxide clusters and that acid treatment has no significant effect on the MOF structure.

3. Page 11-12 line 266-274: As shown in Fig. 4d, the author provided CH3OH yields for reaction temperatures ranging from 25 to 85 °C. Please add the results of solar-to-chemical (STC) energy conversion efficiency at 85 °C in Supplementary Fig. 39.

4. The author provided graphical annotation information for the error bars in both Fig. 4 & 5 of the manuscript, so please be consistent with the manuscript in the appropriate location of the supporting information.

5. Page 10 Fig 4e: As shown in Fig. 4e, with the extension of time CH3OH selectivity is basically maintained at 100%, and the CH3OH yield is slightly decreased, please explain the reason for the decrease in catalytic performance.

6. Page 14 line 347-358: The author assessed the function of iron oxide clusters within the Pd1FeOx/aUiO(H) catalyst by studying the evolution of these species during the PTMO. As shown in Fig. 5f and Supplementary Fig. 52a, compared to Pd1Fe1/aUiO(H), the presence of the CH3 deformation vibrational in Pd1FeOx/aUiO(H) under the same conditions suggests that CH4 can be activated under these conditions. Please supplement the experiment of Pd1Fe1/aUiO(H) in CH4/Ar without H2O and go along with the results of Fig. 5d&Supplementary Fig. 54 to prove the authors' point that iron oxide clusters in the Pd1FeOx/aUiO(H) catalyst could effectively capture photogenerated holes and be oxidized into Fe IV=O species during the PTMO.

7. Zr-O pair shows significant impact on H2 dissociation and C-O bond activation for methanol synthesis (Journal of Energy Chemistry, 2024,93: 126-134; Nature Catalysis, 2022, 5, 818–831). Are there similar effect in C-H activation for synthesizing methanol?

Reviewer #2

(Remarks to the Author)
In this work, the authors develop innovative membrane nanoreactors based on tuned MOF with active Pd1 and Fe1 active sites, promoting a tandem reaction towards the photocatalytic direct oxidation of methane to methanol. These membranes have several tuned properties that allow for: (i) efficient management of reactants and intermediates through a controlled gas-solid interphase; (ii) H2O2 generation from POR promoted by Pd1 active sites in the vicinity of the Fe1 sites; (iii) H2O2-mediated oxidation of methane in the Fe1 sites. In addition, the system leveraged the infrared portion of the solar spectrum to heat the membrane, thus improving the water release from the inner MOF structure, while the authors also demonstrate the possibility to directly use the sunlight and tap water with no negative effect on the photocatalytic performance. The results are definitely impressive and represent a significant advance in the field, thanks to the mentioned aspects not only in terms of functionality but also on the management of reactants and other species through the control of the gas/solid interface.
Before consideration for publication, several minor concerns need to be addressed:
1. The optoelectronic properties of the materials are not investigated in much depth. Only some of the UV-vis spectra are shown. The band diagrams of the materials are not presented.
2. Please explain how the Fe loadings were controlled during photo-deposition. By illumination time?
3. It is recommended to perform 13CH4 experiment to confirm the carbon resource of methanol.
4. I suggest using the same y scale for Figures 4e and 4f for a more straightforward comparison.
5. The leaching of the very low amount of metal sites from the catalysts should be studied (e.g., comparison of metal species contents before and after a long-term catalytic reaction).
6. Please explain more in detail the characterization results of the FeOx/aUiO sample in fig 26. Is this structure actually comparable to the ones obtained on the Pd1/aUiO(H), considering it is a photo-deposition method?
7. In the SI explaining Fig. S19, a plausible explanation of the favored iron oxide clusters in the pores is understood by carrying out photo-deposition with and without a hole scavenger. A short sentence on this could be added to the main text.

Reviewer #3

(Remarks to the Author)
The photocatalytic conversion of methane to methanol is one of the important pathways for methane utilization. This article investigates the photocatalytic oxidation of methane to methanol in an m membrane reactor. The results showed that Pd and Fe synergistically promote the production and utilization of H2O2 at the nodes of MOF. Meanwhile, the MOF ensures efficient gas diffusion and rapid methanol desorption and transfer. Among them, the design of fixing Pd and Fe onto the catalyst to achieve in-situ production of H2O2 and subsequent oxidation of methane to methanol has significant innovation. This is an interesting and meaningful article. However, some revisions are needed.
1. Supplementary Fig. 36 compares the amount of H2O2 remaining in the catalyst membrane under different temperatures, Why do not compares the amount of H2O remaining in the catalyst membrane? If H2O remains in the membrane, the reaction rate will slow down and the advantage of gas-solid interface will disappear.
2. The PTMO involves two steps, the first is the generation of H2O2, and the second is the oxidation of methane by H2O2 to obtain methanol. Systematical experiments have been done. MD simulations also rationalize the experimental observations of the second step (CH4+H2O2→CH3OH), namely the rate at the gas-solid interface is much higher than that at the liquid-solid interface due to the enhanced efficiency of gaseous reactant transfer. However, no theoretical or simulation results were provided to support the first step. If possible, it is better to study the generation mechanism of H2O2 on the employed catalysts.
3. The conclusion emphasizes the advantages of MOF membrane reactor, without mentioning the scientific discoveries obtained regarding the catalytic oxidation of methane to produce methanol. This conclusion thus appears vague.
4. In the MD simulation section, there is too little details about the simulation settings, and of particular is no clear indication of whether the boxes are periodic or not.
5. For an ideal situation, where there is no water interference, the reaction will also produce water (CH4+H2O2→CH3OH+H2O), with a maximum molar ratio of 1:1.They mentioned that they collected high-concentration methanol. What is the concentration of methanol in the mixture?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript has been well revised and improved. I suggest it to be published in nature communications.

Reviewer #2

(Remarks to the Author)
I have carefully read the revised manuscript.I think the authors made efforts to revise the manuscript to address all questions.

I recommend acceptance of the manuscript.

Reviewer #3

(Remarks to the Author)
My concerns have been well addressed.

Response to Reviewers

Reviewer #1:

This paper reported a metal-organic framework (MOF) membrane nanoreactor, by introducing Pd and Fe on the MOF node as POR and HMO sites, achieving high photocatalytic tandem methane oxidation (PTMO) performance at the gas-solid interface. Some results are very interesting and would promote the development of this field. Some revisions are still required before final acceptance, as detailed in the following comments.

Author Reply:

Thanks for the Reviewer's positive comments and support for our work.

We have made careful revisions according to the Reviewers' suggestions to improve the quality of our manuscript. We hope the revised manuscript can address the Reviewers' concerns and be accepted for publication in *Nat. Commun*.

R1Q1. Page 6 line 136-148: The author grafted Pd species onto the Zr–O nodes as POR sites to form the Pd_1/aUiO catalyst, provided the H_2O_2 yield corresponding to the catalysts with different Pd loadings in Supplementary Fig. 12, and noted the difference between Pd_1/aUiO (0.78) and Pd_1/aUiO (0.83) in the manuscript. Please explain the reason for increasing the Pd loading to 0.83 wt.% and why not choose a higher loading of Pd (such as 1 wt.%) for the comparison. The author claimed that "This suggests there were no sufficient bonding sites on Zr–O nodes for additionally anchoring atomically dispersed metal species." Please use the mass of Pd instead of the mass of the catalyst to calculate the yield of H_2O_2 and discuss the relationship between H_2O_2 yield and Pd species.

Author Reply:

Thanks for the Reviewer's kind suggestion.

Our work also synthesized Pd_1/aUiO catalysts with increased Pd loadings (0.91 and 1.1 wt.%, as determined by ICP-AES) to assess their photocatalytic performance in H_2O_2 generation. As shown in **Fig. R1**, we found that increasing the Pd loading from 0.83 wt.% to 1.1 wt.% significantly reduced the H_2O_2 generation activity. This observation suggests that the Pd_1/aUiO catalyst with 0.83 wt.% Pd is closer to the optimal composition compared to those with higher Pd loadings, making it well-suited for investigating the effects of structural evolution in metal species on intrinsic catalytic activity. Thus, we did not present the photocatalytic activity of the Pd_1/aUiO catalyst with Pd loading contents larger than 0.83 wt.%. To provide a clearer understanding of the relationship between Pd loading and H_2O_2 yield, we have supplemented a comparison of H_2O_2 yields for Pd_1/aUiO catalysts with higher Pd loadings (0.91 and 1.1 wt.%) and recalculated the H_2O_2 yield based on the mass of Pd rather than the total catalyst mass in the revised SI (**Supplementary Fig. 12)**.

As confirmed by HAADF-STEM and EXAFS analyses (Supplementary Fig. 10 in the original SI), the Pd species in the Pd_1/aUiO catalyst (0.78 wt.%) were atomically dispersed. When the Pd loading was below 0.78 wt.%, the photocatalytic activity for H_2O_2 generation increased with higher Pd loading, attributed to the growing number of Pd_1 active sites. However, Pd atoms aggregated at higher loading contents of Pd (e.g., 0.83 wt.% or above), forming metallic Pd species. These metallic species exhibited significantly reduced intrinsic activity for O_2 reduction to H_2O_2 (*Nat. Commun.*, 2022, 13, 4737; *Nat. Commun.*, 2021, 12, 2682), resulting in a marked decline in H_2O_2 yield.

Furthermore, through additional density functional theory (DFT) calculations, we have expanded the discussion on the relationship between H_2O_2 yield and Pd species, clarifying why single-atomic Pd (Pd_1) species exhibit optimal intrinsic activity for the reduction of O_2 to H_2O_2 (*see **Fig. R9** in our reply to **R3Q2***).

We have also interposed these discussions in the revised SI accordingly (**Pages 13 and 16**)

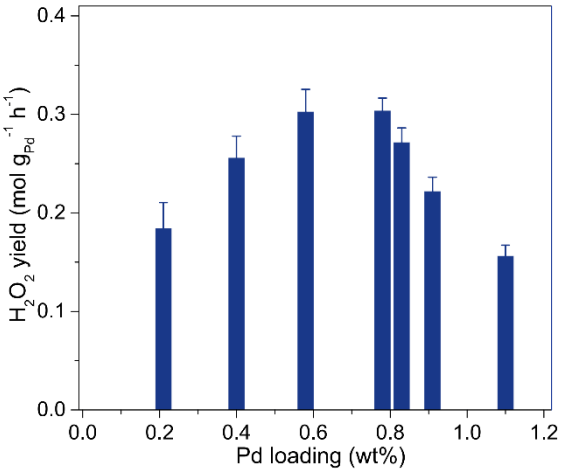

Fig. R1. H_2O_2 yield as a function of Pd loadings in Pd/aUiO catalysts (reaction condition: 80 mL min^{-1} O_2, 25 ^oC, triethanolamine was used as a scavenger for the photogenerated hole).

R1Q2. Page 8 line 174-178: The author showed that the catalyst treated with dilute sulfuric acid showed significant changes in the surface area and pore volume. Please provide the surface area and pore volume results of the Pd_1/aUiO(H), to indicate that this phenomenon is caused by the leaching of iron oxide clusters and that acid treatment has no significant effect on the MOF structure.

Author Reply:

Thanks for the Reviewer's kind reminder.

We have performed BET characterizations for the Pd_1/aUiO(H) catalyst. As shown in **Table R1**, the surface area and pore volume of Pd_1Fe_1/aUiO(H) catalyst closely match those of the Pd_1/aUiO(H) and are significantly higher than those of Pd_1FeO_x/aUiO(H) catalyst. This result indicates that the acid treatment can effectively leach iron oxide clusters (FeO_x) from the Pd_1FeO_x/aUiO(H) catalyst without impacting the pore structure of the MOF substrate.

We have also revised the manuscript accordingly (**Lines 179–181, Page 8**) and inserted **Table R1** in the revised SI (**Supplementary Table 1**).

Table R1. The surface areas and pore volumes of Pd_1FeO_x/aUiO(H), Pd_1Fe_1/aUiO(H), and Pd_1/aUiO(H) samples. The pore size model is "N_2 at 77 K on carbon (slit pore, NLDFT equilibrium model)".

Catalysts	Pore volume ($cm^3\ g^{-1}$)	Surface areas ($m^2\ g^{-1}$)
Pd_1FeO_x/aUiO(H)	0.403	852
Pd_1Fe_1/aUiO(H)	0.420	1060
Pd_1/aUiO(H)	0.421	1068

R1Q3. Page 11-12 line 266-274: As shown in Fig. 4d, the author provided CH_3OH yields for reaction temperatures ranging from 25 to 85 °C. Please add the results of solar-to-chemical (STC) energy conversion efficiency at 85 °C in Supplementary Fig. 39.

Author Reply: Thanks for the Reviewer's kind suggestion. We have added the results for solar-to-chemical (STC) energy conversion efficiency at 85 °C in the revised SI (**Supplementary Fig. 40**).

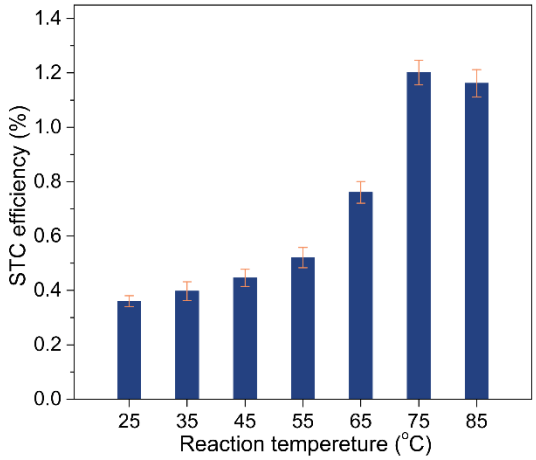

Fig. R2. Solar-to-Chemical (STC) conversion efficiency of Pd_1FeO_x/aUiO(H) membrane under different system temperatures (reaction condition: 150 mL min^{-1} humidified CH_4/O_2 mixture gas). The error bars correspond to the standard deviation of three independent measurements.

R1Q4. The author provided graphical annotation information for the error bars in both Fig. 4 & 5 of the manuscript, so please be consistent with the manuscript in the appropriate location of the supporting information.

Author Reply: Thanks for the Reviewer's kind reminder. We have supplemented the graphical annotation information for the error bars in the revised SI.

R1Q5. Page 10 Fig 4e: As shown in Fig. 4e, with the extension of time CH_3OH selectivity is basically maintained at 100%, and the CH_3OH yield is slightly decreased, please explain the reason for the decrease in catalytic performance.

Author Reply:

Thanks for the Reviewer's kind suggestion.

First, Fe K-edge XAFS results showed no significant changes in the dispersion or electronic structure of the Fe active species within Pd_1FeO_x/aUiO(H) after prolonged reaction (**Supplementary Fig. 56** in the original SI). Additionally, to further evaluate the stability of Pd_1 species during extended catalytic testing, Pd K-edge XAFS characterization was also conducted on the Pd_1FeO_x/aUiO(H) photocatalyst after 210 hours of continuous reaction. As illustrated in **Fig. R3**, the single-atom dispersion and electronic structure of the Pd_1 active species also remained stable over this period. Consequently, the intrinsic catalytic activity of both Pd and Fe species remained unchanged after extensive reaction periods, which accounts for the consistent CH_3OH selectivity, remaining virtually at ~100%.

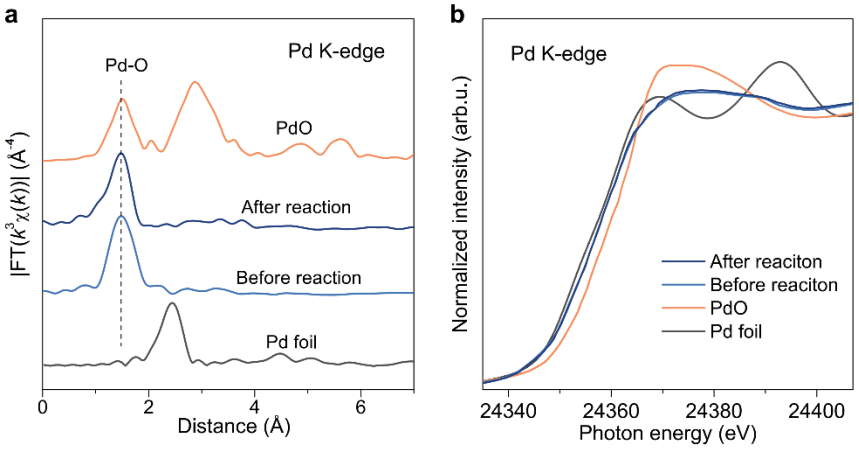

Fig. R3. Characterization of the Pd_1FeO_x/aUiO(H) catalyst after long-term operation (210 h). (**a, b**) Pd K-edge EXAFS spectra (**a**) and XANES spectra (**b**) of Pd_1FeO_x/aUiO(H) catalyst before and after long-term operation.

Additionally, to further explore the reason behind the slight decrease in CH_3OH yield, we have conducted additional characterizations to uncover changes in the structure and photoelectric conversion efficiency of the MOF substrate following long-term reaction periods. As shown in **Fig. R4a**, N_2 sorption isotherms illustrate a slight decline in surface areas and pore volumes after long-term reaction, indicating a minor collapse in the MOF substrate's pore structure. This collapse likely diminishes the photoelectric conversion efficiency of the MOF substrate (as shown in **Fig. R4b**), consequently leading to the observed slight decrease in CH_3OH yield.

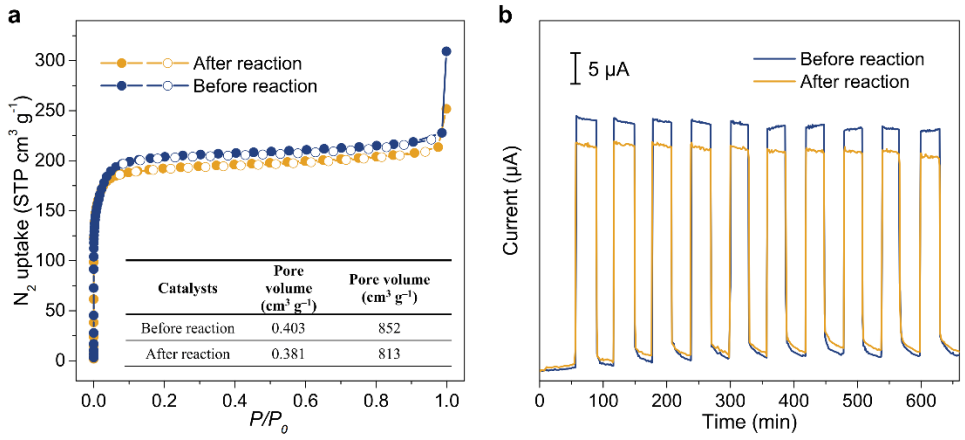

Fig. R4. (**a**) N_2 adsorption-desorption isotherms (at 77 K) and (**b**) photocurrent-time curves under simulated sunlight irradiation for the Pd_1FeO_x/aUiO(H) catalyst before and after long-term operation (210 h).

We have also revised the manuscript accordingly (**Lines 294–296, Page 12**) and inserted **Figs. R3 and R4** in the revised SI (**Supplementary Figs. 45 and 60**). We hope these revisions can address the Reviewer's concerns.

R1Q6. Page 14 line 347-358: The author assessed the function of iron oxide clusters within the Pd_1FeO_x/aUiO(H) catalyst by studying the evolution of these species during the PTMO. As shown in Fig. 5f and Supplementary Fig. 52a, compared to Pd_1Fe_1/aUiO(H), the presence of the CH_3 deformation vibrational in Pd_1FeO_x/aUiO(H) under the same conditions suggests that CH_4 can be activated under these conditions. Please supplement the experiment of Pd_1Fe_1/aUiO(H) in CH_4/Ar without H_2O and go along with the results of Fig. 5d&Supplementary Fig. 54 to prove the authors' point that iron oxide clusters in the Pd_1FeO_x/aUiO(H) catalyst could effectively capture photogenerated holes and be oxidized into Fe^{IV}=O species during the PTMO.

Author Reply:

Thanks for the Reviewer's kind suggestion.

As shown in **Fig. R5**, we have supplemented the in situ ATR-FTIR experiment of the Pd_1Fe_1/aUiO(H) catalyst under CH_4/Ar conditions without H_2O. Notably, under light irradiation, no CH_3 deformation vibrational signal (at ~1471 cm^{-1}) and high-valence Fe^{IV}=O species could be detected on the Pd_1Fe_1/aUiO(H) when using a dry CH_4/Ar mixture as the feed gas. These observations, in conjunction with the findings presented in Fig. 5d and Supplementary Fig. 54 (in the original SI), strongly suggest that the iron oxide clusters (FeO_x) within the Pd_1FeO_x/aUiO(H) catalyst could effectively capture photogenerated holes and be oxidized into Fe^{IV}=O active species during the PTMO process.

We have also revised the manuscript accordingly (**Line 365, Page 14**) and inserted **Fig. R5** in the revised SI (**Supplementary Fig. 58**).

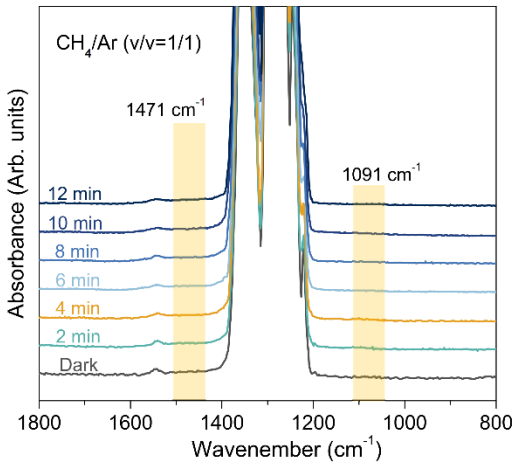

Fig. R5. In situ ATR-FTIR spectra of Pd_1Fe_1/aUiO(H) catalyst under anhydrous CH_4/Ar conditions.

R1Q7. Zr-O pair shows significant impact on H_2 dissociation and C-O bond activation for methanol synthesis (Journal of Energy Chemistry, 2024,93: 126-134; Nature Catalysis, 2022, 5, 818–831). Are there similar effect in C-H activation for synthesizing methanol?

Author Reply:

Thanks for the Reviewer's kind reminder.

In the studies referenced by the Reviewer (*Journal of Energy Chemistry*, 2024, 93, 126; *Nature Catalysis*, 2022, 5, 818), zirconia substrates play a critical role in facilitating high dispersion of Cu active species and modulating their electronic structure to enhance H_2 dissociation and C–O bond activation. Similarly, in our work, the Zr–O nodes within the MOF framework enable atomic dispersion of Pd and Fe active species, effectively tuning their electronic properties to promote H_2O_2 generation and C–H activation, respectively. However, these Zr–O pairs are not directly involved in C–H activation or methanol production. As shown in Supplementary Figure 24 in our original SI, we carefully evaluated the PTMO performance of the Pd_1/aUiO(H) catalyst and observed only negligible methane oxidation activity, producing minimal methanol. This finding indicates that CH_4 molecules cannot be efficiently activated and converted to CH_3OH without the presence of active Fe species (i.e., Fe_1 and FeO_x).

We have inserted these two references (*Journal of Energy Chemistry*, 2024, 93, 126; *Nature Catalysis*, 2022, 5, 818) into the revised manuscript (Ref. 46 and 47) to better clarify the role of the Zr–O pairs. We hope these explanations can address the Reviewer's concerns.

Reviewer #2:

In this work, the authors develop innovative membrane nanoreactors based on tuned MOF with active Pd1 and Fe1 active sites, promoting a tandem reaction towards the photocatalytic direct oxidation of methane to methanol. These membranes have several tuned properties that allow for: (i) efficient management of reactants and intermediates through a controlled gas-solid interphase; (ii) H_2O_2 generation from POR promoted by Pd_1 active sites in the vicinity of the Fe1 sites; (iii) H_2O_2-mediated oxidation of methane in the Fe_1 sites. In addition, the system leveraged the infrared portion of the solar spectrum to heat the membrane, thus improving the water release from the inner MOF structure, while the authors also demonstrate the possibility to directly use the sunlight and tap water with no negative effect on the photocatalytic performance. The results are definitely impressive and represent a significant advance in the field, thanks to the mentioned aspects not only in terms of functionality but also on the management of reactants and other species through the control of the gas/solid interface. Before consideration for publication, several minor concerns need to be addressed.

Author Reply:

Thanks for the Reviewer's positive comments and support for our work.

To further improve the quality of our manuscript and address your concerns, we have made careful revisions according to each comment of the Reviewers. We hope the revised manuscript can address the concerns of the Reviewers and meet the high standard required for publication in *Nat. Commun*.

R2Q1. The optoelectronic properties of the materials are not investigated in much depth. Only some of the UV-vis spectra are shown. The band diagrams of the materials are not presented.

Author Reply:

Thanks for the Reviewer's kind suggestion.

We have carried out more characterizations to reveal the energy band structure of the as-obtained photocatalyst. As shown in **Fig. R6a**, the band gap for aUiO is about 2.46 eV. From the UPS valence-band spectra (**Fig. R6b, c**), the HOMO energy level of aUiO can be calculated to be −6.36 eV relative to the vacuum level (*ACS Nano*, 2014, 8, 8582; *Adv. Mater*, 2016, 28, 6959). That is, the HOMO energy level for aUiO is 1.86 eV versus the normal hydrogen electrode (NHE). Given the obtained bandgaps of 2.46 eV (**Fig. R6a**), the conduction band (i.e., LUMO) potential for aUiO is then calculated to be −0.60 V vs. NHE (**Fig. R6d**).

We have also revised the manuscript accordingly (**Line 89, Page 4**) and inserted **Fig. R6** in the revised SI (**Supplementary Fig. 3**).

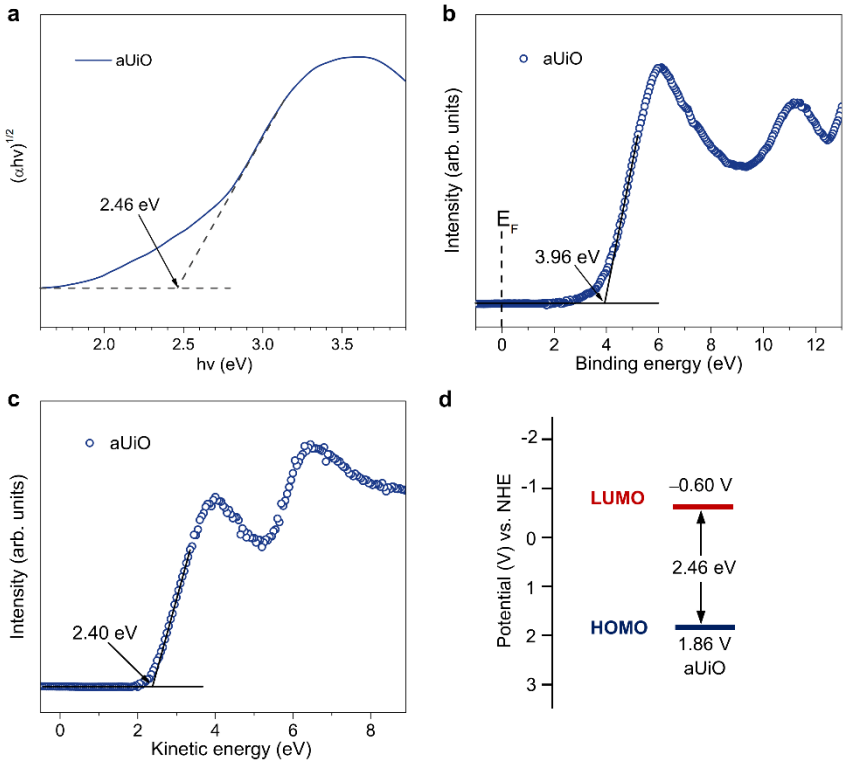

Fig. R6. **Electronic band structure of the aUiO sample.** (**a**) Optical band gap determined by UV-vis diffuse reflectance, where α and ν represent the absorbance and wavenumber, respectively. (**b**) Valence-band spectra for aUiO measured by ultraviolet photoelectron spectroscopy (UPS). Au serves as a reference for E_F set to 0 eV. (**c**) Secondary electron cutoff (E_{cutoff}) in the UPS spectra can be calculated from the work function (Φ). (**d**) Schematic diagrams for conduction band gap of the aUiO.

R2Q2. Please explain how the Fe loadings were controlled during photo-deposition. By illumination time?

Author Reply:

Thanks for the Reviewer's kind suggestion.

In this work, we controlled the Fe loadings by regulating the concentration of the precursor solution. For instance, to synthesize Pd_1FeO_x/aUiO(H) catalysts with Fe loadings of 0.23, 0.45, 0.67, 0.89, 1.06 wt.%, we injected 0.45, 0.9, 1.35, 1.8, and 2.15 mL of a 5 mM $FeCl_3$ aqueous solution as the precursor.

We have also supplemented the experimental detail in the "Methods" section of the revised manuscript accordingly (**Lines 437–440, Page 17**). We hope these revisions can address the Reviewer's concerns.

R2Q3. It is recommended to perform $^{13}CH_4$ experiment to confirm the carbon resource of methanol.

Author Reply:

Thanks for the Reviewer's kind suggestion.

We have performed the $^{13}CH_4$ experiment, as shown in **Fig. R7**, confirming that the carbon source of the produced methanol is derived from methane molecules.

We have also revised the manuscript accordingly (**Lines 280–283, Page 12**) and inserted **Fig. R7** in the revised SI (**Supplementary Fig. 41**).

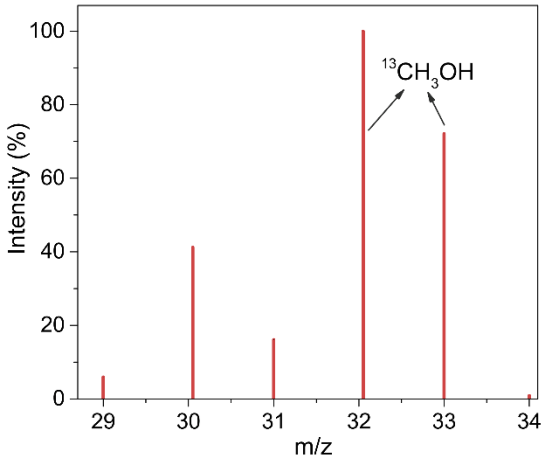

Fig. R7 Mass spectra of the product $^{13}CH_3OH$ from $^{13}CH_4$ photo-oxidation by the Pd_1FeO_x/aUiO(H) membrane.

R2Q4. I suggest using the same y scale for Figures 4e and 4f for a more straightforward comparison.

Author Reply:

Thanks for the Reviewer's kind suggestion.

We have adjusted the y scale of Figures 4e and 4f in the revised manuscript for a clearer comparison.

R2Q5. The leaching of the very low amount of metal sites from the catalysts should be studied (e.g., comparison of metal species contents before and after a long-term catalytic reaction).

Author Reply:

Thanks for the Reviewer's kind suggestion.

We have conducted ICP-AES characteristics to compare the contents of metal active species before and after the long-term catalytic reaction. **Table R2** shows minimal leaching of metal sites after the long-term reaction, indicating the ultrahigh stability of Pd_1FeO_x/aUiO(H) catalyst.

Table R2. ICP analysis of Pd_1FeO_x/aUiO(H) photocatalyst membrane before and after PTMO reactions.

Reaction time (hour)	Loading (wt.%)	
	Pd	Fe
0	0.78	0.89
100	0.78	0.89
210	0.78	0.88

We have also revised the manuscript accordingly (**Lines 294–296, Page 12**) and inserted **Table R2** in the revised SI (**Supplementary Table 5**).

R2Q6. Please explain more in detail the characterization results of the FeO_x/aUiO sample in fig 26. Is this structure actually comparable to the ones obtained on the Pd_1/aUiO(H), considering it is a photo-deposition method?

Author Reply:

Thanks for the Reviewer's kind suggestion.

Actually, the FeO_x/aUiO designation refers to the aUiO substrate modified with both single-atom Fe (Fe_1) and FeO_x clusters. This structure is comparable to the Pd_1FeOx/aUiO catalyst, derived from Pd_1/UiO(H), but without modifying Pd_1 active sites.

We have provided detailed explanations of the characterization results for the FeO_x/aUiO catalyst in the revised SI (**Page 28**). We hope these revisions can address the Reviewer's concerns.

R2Q7. In the SI explaining Fig. S19, a plausible explanation of the favored iron oxide clusters in the pores is understood by carrying out photo-deposition with and without a hole scavenger. A short sentence on this could be added to the main text.

Author Reply:

Thanks for the Reviewer's kind suggestion.

In the revised manuscript, we have added a short sentence, "*Additionally, when the hole scavenger was introduced during the photo-deposition process, it resulted in the exclusive integration of atomically dispersed Fe species into aUiO(H), with iron oxide clusters being notably absent in the resultant sample.*" (**Lines 191–193, Page 8**).

Reviewer #3:

The photocatalytic conversion of methane to methanol is one of the important pathways for methane utilization. This article investigates the photocatalytic oxidation of methane to methanol in an m membrane reactor. The results showed that Pd and Fe synergistically promote the production and utilization of H_2O_2 at the nodes of MOF. Meanwhile, the MOF ensures efficient gas diffusion and rapid methanol desorption and transfer. Among them, the design of fixing Pd and Fe onto the catalyst to achieve in-situ production of H_2O_2 and subsequent oxidation of methane to methanol has significant innovation. This is an interesting and meaningful article. However, some revisions are needed.

Author Reply:

Thanks for the Reviewer's positive comments on our work.

To further improve the quality of our manuscript and address your concerns, we have made careful revisions according to each comment of the Reviewers. We hope the modifications will address the Reviewers' concerns and fulfill the rigorous criteria for publication in *Nat. Commun.*

R3Q1. Supplementary Fig. 36 compares the amount of H_2O_2 remaining in the catalyst membrane under different temperatures, why do not compares the amount of H_2O remaining in the catalyst membrane? If H_2O remains in the membrane, the reaction rate will slow down and the advantage of gas-solid interface will disappear.

Author Reply:

Thanks for the Reviewer's instructive suggestions.

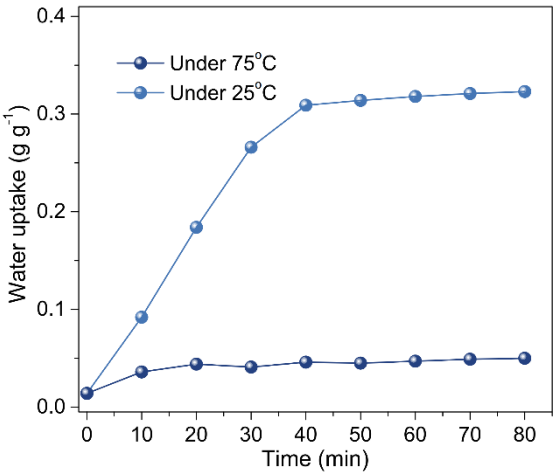

Fig. R8. Comparison of the amount of H_2O remaining in the Pd_1FeO_x/aUiO(H) membrane under different system temperatures (reaction condition: 150 mL min^{-1} humidified CH_4/O_2 mixture gas).

According to the Reviewer's suggestion, we monitored residual H_2O in the catalyst membrane during the PTMO process at both ambient (25°C) and elevated (75°C) temperatures. As shown in **Fig. R8**, water vapor from the humidified feed gas was retained within the MOF pores during the PTMO process at ambient

temperature (25°C). As expected, increasing the temperature of the MOF membrane nanoreactor to 75°C enhanced water vapor diffusion through the MOF pores, significantly reducing water retention and condensation at the gas-solid catalytic interface.

We have also revised the manuscript accordingly (**Lines 263–266, Page 11**) and inserted **Fig. R8** in the revised SI (**Supplementary Fig. 37a**).

R3Q2. The PTMO involves two steps, the first is the generation of H_2O_2, and the second is the oxidation of methane by H_2O_2 to obtain methanol. Systematical experiments have been done. MD simulations also rationalize the experimental observations of the second step ($CH_4+H_2O_2 \rightarrow CH_3OH$), namely the rate at the gas-solid interface is much higher than that at the liquid-solid interface due to the enhanced efficiency of gaseous reactant transfer. However, no theoretical or simulation results were provided to support the first step. If possible, it is better to study the generation mechanism of H_2O_2 on the employed catalysts.

Author Reply:

Thanks for the Reviewer's instructive suggestions.

In this study, we selected Pd species to functionalize Zr–O nodes as POR sites because of their proven ability to catalyze O_2 hydrogenation to generate H_2O_2 in both thermocatalysis and photocatalysis (*Nat. Commun.*, 2022, 51, 4737; *J. Am. Chem. Soc.*, 2023, 145, 19877). To further elucidate why single-atom Pd (Pd_1) was chosen over conventional Pd nanoparticle as H_2O_2 generation active center, we have performed first-principles calculations to investigate the formation of H_2O_2 over Pd single atom and nanoparticle. The Pd_1/aUiO(H) model is based on the palladium-oxygen coordination number fitted by EXAFS (**Fig. R9a**), and the Pd nanoparticle is extracted from the bulk phase of Pd (111) (**Fig. R9b**).

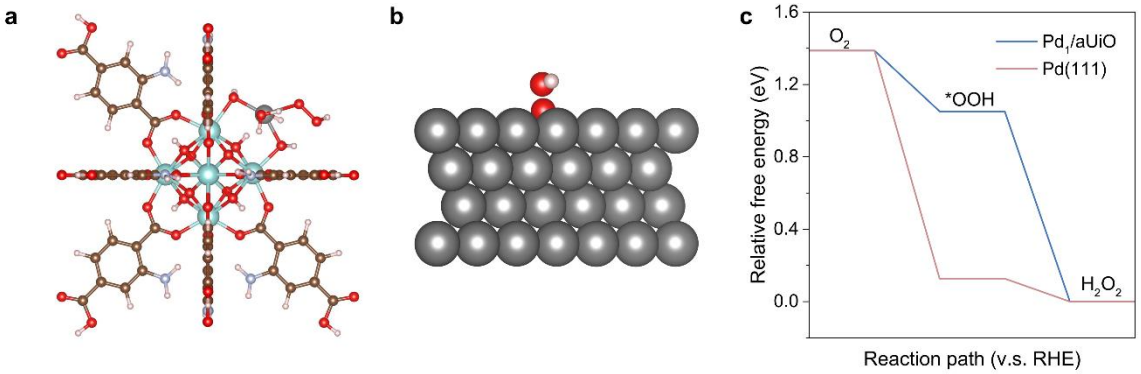

Fig. R9. (**a**, **b**) Side views of the slab models for Pd_1/aUiO and Pd (111) facets, respectively. (**c**) Calculated potential energy diagrams for hydrogenation of O_2 to H_2O_2 on Pd_1 sites and Pd (111) surfaces.

As shown in **Fig. R9c**, the rate-determining step (RDS) for O_2 reduction to generate H_2O_2 on Pd_1 sites of Pd_1/aUiO(H) is the formation of *OOH from adsorbed O_2, with a step free energy drop of 0.336 eV. In contrast, on the surface of Pd nanoparticles, the RDS is the hydrogenation of *OOH, which exhibits a

smaller step free energy drop of 0.127 eV. Compared to Pd nanoparticles, Pd_1 sites effectively regulate the free energy differences at each reaction step by weakening the adsorption strength of *OOH, thereby facilitating the reaction. Overall, these calculated results suggest that Pd_1 sites are significantly more favorable than conventional Pd nanoparticles for H_2O_2 generation.

We have also revised the manuscript accordingly (**Lines 146–148, Page 6**) and inserted **Fig. R9** in the revised SI (**Supplementary Fig. 15**).

R3Q3. The conclusion emphasizes the advantages of MOF membrane reactor, without mentioning the scientific discoveries obtained regarding the catalytic oxidation of methane to produce methanol. This conclusion thus appears vague.

Author Reply:

Thanks for the Reviewer's instructive suggestions.

To emphasize the scientific breakthroughs in the photocatalytic oxidation of methane to methanol, we revised our conclusion as follows: "*In summary, we have developed a proof-of-concept MOF membrane nanoreactor by assembling MOF crystals (NH_2-UiO-66) decorated by sterically colocalized single-atom palladium (Pd_1) and iron (Fe_1) onto a gas diffusion layer. We show that the PTMO could be boosted at the gas-solid interface by maximizing the spatial intimacy of the photocatalytic H_2O_2 generation (Pd_1) and CH_4 oxidation (Fe_1) sites, thereby effectively circumventing H_2O_2 dilution. Moreover, photothermal effect-driven interfacial water management enables the simultaneous effective desorption of hydrophilic CH_3OH and high-flux diffusion of hydrophobic CH_4 within the MOF membrane nanoreactor. Consequently, this MOF membrane nanoreactor demonstrates unprecedented catalytic activity and stability for directly converting methane to high-concentration methanol under simulated sunlight irradiation. Moreover, our MOF membrane nanoreactor represents a photocatalytic platform with both scientific value and practical application potential for a wide range of three-phase photocatalytic reactions. The powerful toolbox in single-atom catalysis and MOF chemistry endows us with almost infinite possibilities to tune the chemical compositions and pore microenvironments of MOF, enabling the design of specialized MOF membrane nanoreactors optimized for diverse three-phase tandem catalytic reactions and facilitating the investigation of these reactions' mechanisms at an atomic level. The facile preparation of hybrid MOF membranes, the easy scale-up of such photocatalysis devices, and the minimized usage of moisture (instead of freshwater) make them even more suitable for applications in regions with limited access to pure water and abundant solar energy.*" (**Lines 383–401, Page 15)**

We hope these revisions can address the Reviewer's concerns.

R3Q4. In the MD simulation section, there is too little details about the simulation settings, and of particular is no clear indication of whether the boxes are periodic or not.

Author Reply:

Thanks for the Reviewer's instructive suggestions.

In our molecular dynamics simulations, we have indeed employed periodic boundary conditions (PBCs). This means that the simulation box is periodic in all three spatial dimensions, allowing molecules to seamlessly pass through the boundaries of the simulation box as if traversing an infinitely repeating structure.

We recognize that the original manuscript did not explicitly state this, which may have caused some ambiguity. To address this, we have revised the simulation settings section in the revised manuscript to clarify these aspects, ensuring readers have a precise understanding of our research methodology (**Lines 605–622, Page 21**).

R3Q5. For an ideal situation, where there is no water interference, the reaction will also produce water ($CH_4+H_2O_2 \rightarrow CH_3OH+H_2O$), with a maximum molar ratio of 1:1.They mentioned that they collected high-concentration methanol. What is the concentration of methanol in the mixture?

Author Reply:

Thanks for the Reviewer's valuable questions.

As described in our manuscript, the concentration of the collected methanol is approximately 0.25 moles per liter (0.25 M), which is significantly lower than the ideal level (achievable without water interference). This reduced concentration is primarily attributed to the abundant water vapor in the feed gas, which has been proven critical for enabling an efficient and selective PTMO process to generate methanol. On one hand, water vapor can promote the effective desorption of generated methanol. Thus, to prevent overoxidation, the PTMO system should enable the continuous sweeping of the MOF catalyst layer with high-throughput water vapor to promote the transfer of methanol. On the other hand, water also serves as a crucial reactant in the PTMO process, facilitating the formation of active Fe^{IV}=O species on FeO_x clusters under light irradiation. Consequently, an ample supply of water vapor enhances the efficient oxidative dehydrogenation of methane, thereby promoting effective methanol generation.

Response to Reviewers

Reviewer #1:

The manuscript has been well revised and improved. I suggest it to be published in nature communications.

Author Reply:

We are very grateful to your encouraging and positive comments and really appreciate your agreement of acceptance with this revised manuscript.

Reviewer #2:

I have carefully read the revised manuscript. I think the authors made efforts to revise the manuscript to address all questions.

I recommend acceptance of the manuscript.

Author Reply:

We appreciate the Reviewer's recommendation of acceptance and helpful comments in the reviewing process. We are very pleased to have our manuscript reviewed by the Referee.

Reviewer #3:

My concerns have been well addressed.

Author Reply:

We are very grateful to your encouraging and positive comments and really appreciate your agreement of acceptance with this revised manuscript.