

Rh³⁺ stabilized in KRh@MFI catalyses regioselective hydroformylation

Corresponding Author: Dr Avelino Corma

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

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

Zhao et. al, reported K-Rh@MFI catalyst with high hydroformylation performance. By changing the pretreatment with H₂-CO or syngas, the authors demonstrated that Rh³⁺ are responsible for hydroformylation while Rh⁺ is accounting for the isomerization. With this observation, the authors found that by adding a certain number of organic additives like NMP or MP, which can significantly increase the l/b ratio by blocking the Rh⁺ sites. The whole paper has a clear outline and the results are exciting with a state-of-the-art l/b ratio (817) by modifying the Rh⁺ species. However, a few significant concerns weaken the claims. Substantial improvement is required before this work can be considered for publication in Nature or other journals.

1) The authors claim that Rh⁺ species can be generated via H₂ pretreatment at 600 °C for 3 h followed by CO treatment at 90 °C for 2 h (denoted as KRh@MFI-CalRed-CO). In contrast, the sample pretreated under 40 bar CO/H₂ in toluene (KRh@MFI-Cal-Toluene-CO/H₂) is described as predominantly containing isolated Rh³⁺ sites. However, the CO-FTIR results appear to contradict this assignment, as the intensity of the Rh⁺-associated bands remains higher than that of Rh³⁺ in the latter sample. Given this discrepancy, it is unclear how the authors justify assigning this sample as Rh³⁺-dominant. A more quantitative analysis, such as estimating the Rh³⁺/Rh⁺ ratio from spectroscopic data, would significantly strengthen this claim.

2) Furthermore, for the KRh@MFI-Cal-Toluene-CO/H₂ sample, only CO-FTIR characterization is presented. Additional complementary techniques (e.g., XAS, H₂-TPR) would be highly valuable to corroborate the proposed oxidation state and coordination environment of Rh species.

3) A related concern arises from the intrinsic reaction rate (R₀) for isomerization. The Rh³⁺-enriched sample (KRh@MFI-Cal-Toluene-CO/H₂) exhibits an R₀ that is approximately two orders of magnitude lower than that of the Rh⁺-rich sample (KRh@MFI-CalRed-CO).

I wonder how would the activity and linear-to-branched (l/b) ratio evolve upon additive incorporation in the Rh³⁺ system? Such comparisons could help clarify whether the additive effect is specific to Rh⁺ sites or more general.

4) More generally, the conclusions regarding the distinct roles of Rh³⁺ and Rh⁺ species in governing l/b ratio are compared in MFI zeolite. Was this conclusion also can be applied in to some other topologies like FAU or FER.

5) The authors report a significant increase in the linear-to-branched (l/b) ratio (from 20 up to 378 or higher) upon addition of organic additives, which is attributed to modification of the electronic properties of Rh⁺ species. Ex situ IR spectra (Figure 2i, B and C) indeed show clear differences between catalysts used w/ and w/o MP.

To further substantiate this interpretation, it would be highly valuable to perform in situ CO-FTIR measurements under reaction-relevant conditions with gradual co-feeding of MP. If the proposed electronic modulation of Rh⁺ is correct, one might expect a measurable shift (e.g., red shift) in the Rh⁺-CO stretching frequencies. Such data would provide more direct evidence for the proposed mechanism.

6) The optimization of the MP/Rh ratio (reported as 500) raises an additional question. As shown in Table S8, increasing the MP/Rh ratio leads to a decrease in catalytic rate. If MP primarily acts by selectively blocking or modifying Rh⁺ sites, one might expect the reaction rate to remain relatively constant beyond a certain threshold. However, the observed rate suppression therefore suggests that MP may also influence substrate accessibility, active site availability, or reaction kinetics in a more complex manner. The authors should explain more about this point. Also, it would be interesting to explore the extreme case where MP is used as the solvent. How would the catalytic activity and l/b ratio behave under such

conditions?

7) For Table S8, when MP/Rh=4000 (entry 5). The reported aldehyde yield (54.1%) appears inconsistent with the product of the given conversion and selectivity ($84.4\% \times 89.7\%$). The authors are requested to clarify this discrepancy and provide the calculation formulas in the Supporting Information.

8) For the TON calculation, the number of Rh active sites should be reconsidered, as the MP blocks the Rh⁺ sites.

9) I recommend the author can test hydroformylation of cyclohexene and allylbenzene. What would the rates and l/b rate change w/ and w/o MP additives.

10) Minor points. Some figures in SI were not mentioned in manuscript like FigureS1, S39. The authors should either reference these figures where relevant or remove them if they do not contribute to the key conclusions.

Referee #2

(Remarks to the Author)
see attached file

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

Zhao et al. have submitted a revised manuscript focusing on olefin hydroformylation catalyzed by K-Rh@MFI composites. I appreciate the authors' detailed point-by-point response to previous reviewer comments as well as the substantial supplementary experimental data added in this revised version, which fully reflects the authors' dedicated efforts to address all prior concerns raised in the first round of review. Nevertheless, several critical scientific issues still remain unresolved. Despite the noticeable improvement of this manuscript, further targeted revisions are still indispensable to consolidate the research conclusions and meet the rigorous publication standards of Nature.

1. Supplementary catalytic performance comparison. The authors have not provided comparative hydroformylation results of Rh@FER catalysts with and without NMP additives. Given that the authors attribute catalytic differences to zeolite channel size effects, supplementary catalytic tests of Rh@FER with and without MP additives are highly required for systematic validation.

2. Lack of CO-IR characterization evidence. The authors have synthesized and compared Rh-based catalysts supported on zeolites with diverse topological structures. However, CO infrared spectroscopy (CO-IR), the most direct and convincing characterization technique to verify the blocking effect toward Rh⁺ active sites, is absent in this work. Supplemental CO-IR spectra will provide solid spectroscopic evidence to support the authors' core hypothesis of Rh⁺ site blocking.

3. Verification of Rh dispersion via CO chemisorption. To reliably validate the claimed 100% dispersion of rhodium species on the support, CO chemisorption tests are suggested. At minimum, such measurements should be conducted on the pristine additive-free Rh@MFI catalyst to quantify the actual metal dispersion.

4. Simplification of catalyst nomenclature. The current complex naming rules for catalysts severely hinder manuscript readability. Representative complicated labels including KRh@MFI-CalRed-CO and KRh@MFI-Cal-Toluene-CO/H₂ bring unnecessary obstacles for readers to distinguish different catalyst samples. The authors are suggested to adopt a more concise and unified naming system to clarify sample differences and improve the overall readability of the full text.

5. Mechanistic discussion on excessive MP dosage. As listed in Table S8, the optimal MP/Rh molar ratio for achieving the highest linear-to-branched aldehyde (l/b) ratio ranges from 500 to 1000. If the N-methyl functional group of MP molecules indeed coordinates with Rh⁺ active sites as proposed, the requirement for such a huge excess of MP cannot be reasonably explained. It is recommended to conduct CHNS elemental analysis on spent catalysts to quantify the residual MP content, and further calculate the actual MP/Rh molar ratio after catalyst preparation and catalytic reactions, so as to clarify the coordination mechanism between MP and Rh active centers.

6. EXAFS spectra fitting and structural parameter analysis. The Rh K-edge EXAFS spectra displayed in Figure 2h and Figure S59b cover three key samples: post-reaction KRh@MFI-Cal, post-reaction KRh@MFI-Cal-500MP, and CO-treated KRh@MFI-CalRed-CO. All these EXAFS curves need to be quantitatively fitted to extract key structural parameters, including coordination number, interatomic distance and Debye-Waller factor. The fitting results will help elucidate the detailed local coordination environment of Rh active centers, especially the Rh-O and Rh-C coordination shells around rhodium sites if possible.

Referee #2

(Remarks to the Author)

The authors have put a lot of effort to answer many questions raised by the reviewers, and the manuscript has certainly significantly improved. Further improvements are still required before possible publication in Nature.

In contrast to the answer of the authors, I could not find any information about the enthalpies, only Gibbs free energy (Table S5 and S6 and associated figure). The Reviewer thinks it is essential to provide both considering that entropy is very difficult to calculate and the actual energy landscape likely lies in between these two values; it is also a good way to gauge how much entropy is driving the processes.

The authors have clarified the mechanism; the Reviewer thinks it is important to highlight in the main text the change of reaction mechanism with Rh(III) intermediates; favoring sigma-bond metathesis over oxidative addition (as observed for Rh(I)); this will be particularly valuable for the readers in molecular chemistry, which may decide to design novel systems based on this work

Based on the answer of the authors; the reviewer was puzzled by the assignment of some of the Rh(CO) surface sites to Rh(II) species, while it is not discussed (and evaluated) in the XANES section. This needs to be clarified why it is not included in the XANES analysis if it is inferred according to IR. Any other interpretation ? Any other evidence for Rh(II), like EPR?

In addition the IR signatures of few (some fully characterized) Rh(III) carbonyl have been discussed in the literature, e.g. New J. Chem., 2024, 48, 18365-18375; Inorg. Chem. 2003, 42, 3801–3814; JOMC 1979, 165, 93. Their IR signatures seem to be close in some cases to the Rh(II) species discussed above. Some would be nice references for XANES. The authors should consider these references to further support their interpretation.

Minor comments: The Reviewer feels that the quality of the Figures could be improved ; most figures look a bit crude considering what can be done nowadays with computer graphics.

Version 2:

Reviewer comments:

Referee #1

(Remarks to the Author)

The authors have improved the paper according to the review comments. I believe this work constitutes a significant contribution to hydroformylation catalysis, and therefore, I recommend its publication in Nature.

Referee #2

(Remarks to the Author)

The authors have improved the manuscript, which is probably suitable for publications.

See below some minor comments and corrections.

- 1) The authors used the term H₂ adsorption, while it is probably better to use the term H₂ coordination
- 2) In ESI, the Tables with enthalpies and Gibbs free energies are presented in a sub-optimal way as it is difficult to easily assess the impact of entropy. The two tables could be merged with Gibbs free energy and Enthalpy values provided side by side, for instance as follows; DeltaG (DeltaH) for each step and TS as it allows to directly assess the impact of entropy without the need to look at two Tables. Also providing both values in (the) a Figure (potential energy surface) would be helpful.
- 3) As pointed out in my previous report, the Schemes and Figures could be improved (e.g. the use of times or related font for Scheme and to draw molecules is often not ideal); it is a matter of taste and policies but anything making figures appealing is a plus.

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The authors appreciate the referee's effort and time for the critical review of the manuscript. The manuscript has been updated with new information and a point to point answer to all the comments risen by the referees is included in this document in red color.

All changes done in the manuscript are marked in red in the revised version.

Referee #1

Comments:

Zhao et. al, reported K-Rh@MFI catalyst with high hydroformylation performance. By changing the pretreatment with H₂-CO or syngas, the authors demonstrated that Rh³⁺ are responsible for hydroformylation while Rh⁺ is accounting for the isomerization. With this observation, the authors found that by adding a certain number of organic additives like NMP or MP, which can significantly increase the l/b ratio by blocking the Rh⁺ sites. The whole paper has a clear outline and the results are exciting with a state-of-the-art l/b ratio (817) by modifying the Rh⁺ species. However, a few significant concerns weaken the claims. Substantial improvement is required before this work can be considered for publication in Nature or other journals.

Response: We sincerely thank the reviewer for the positive and encouraging evaluation of our work, and appreciate the recognition of its significance in the field.

1) The authors claim that Rh⁺ species can be generated via H₂ pretreatment at 600 °C for 3 h followed by CO treatment at 90 °C for 2 h (denoted as KRh@MFI-CalRed-CO). In contrast, the sample pretreated under 40 bar CO/H₂ in toluene (KRh@MFI-Cal-Toluene-CO/H₂) is described as predominantly containing isolated Rh³⁺ sites. However, the CO-FTIR results appear to contradict this assignment, as the intensity of the Rh⁺-associated bands remains higher than that of Rh³⁺ in the latter sample. Given this discrepancy, it is unclear how the authors justify assigning this sample as Rh³⁺-dominant. A more quantitative analysis, such as estimating the Rh³⁺/Rh⁺ ratio from

spectroscopic data, would significantly strengthen this claim.

Response: Following the reviewer's suggestion, a quantitative comparison of the ratio $\text{Rh}^{3+}/\text{Rh}^+$ was attempted, which is now included in the revised manuscript as Appendix 4.3 in Supporting Information.

Quantifications of Rh^+ and Rh^{3+} species, requires determination of IR extinction coefficients for $\text{Rh}^+(\text{CO})_2$ and $\text{Rh}^{3+}(\text{CO})$ IR bands. We did a semi-quantitative estimation correlating the intensity of the $\text{Rh}^+(\text{CO})_2$ and $\text{Rh}^{3+}(\text{CO})$ IR bands with the Rh loading of pre-selected reference compounds, assuming that all Rh of our compound is interacting with CO and that the IR spectra correspond to maxima CO surface coverage.

The experimental procedure used is detailed below:

The Beer-Lambert Law is usually used to estimate the extinction coefficient (ϵ)¹:

$$n = \frac{A \cdot S}{\epsilon \cdot m}$$

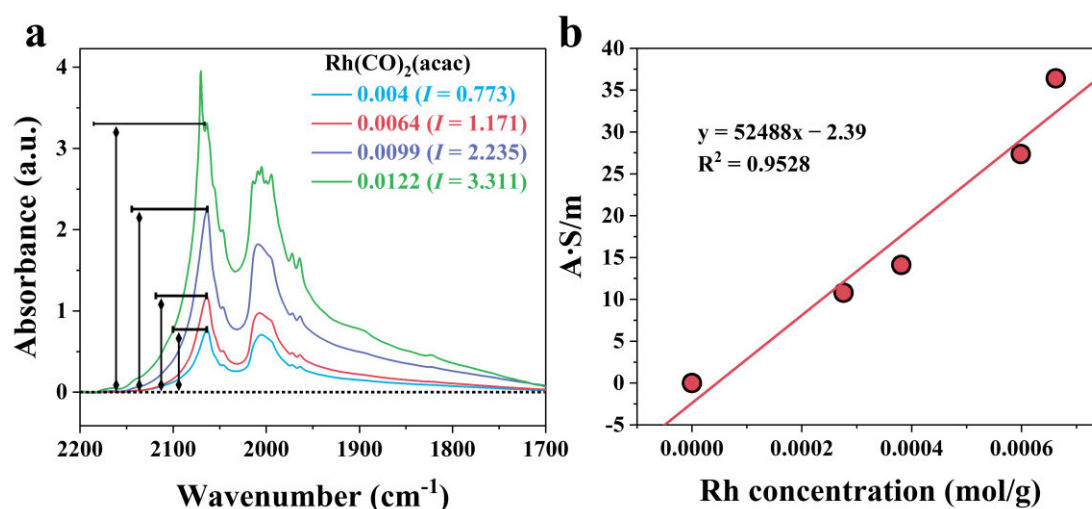
Where n stands for the Rh concentration (mol/g); A is the integrated absorbance area (cm^{-1}) or absorbance intensity (a.u.); S represents the surface area of pellets (cm^2); ϵ is the extinction coefficient (cm/mol); and m stands for the weight of pellet (g).

For the case of Rh^+ we used different amounts of $\text{Rh}(\text{CO})_2(\text{acac})$ (Sigma-Aldrich, 98% purity) mixed with KBr and pressed into 10 mm diameter pellets. For calculations, we used the intensity of the peak at 2064 cm^{-1} corresponding to the ν_{as} vibration of the dicarbonyl specie interacting with Rh^+ .

The corresponding data are included in Table R1 and plotted in Figure R1.

Table R1. Rh^+ (CO)₂ peak intensity and correlation with Rh^+ amount

Samples $\text{Rh}(\text{CO})_2(\text{acac})$ weight (g)	KBr weight (g)	(m) Pellet weight (g)	Rh concentration ($\times 10^{-3}$ mol/g)	(A) IR $\text{Rh}^+(\text{CO})_2$ intensity (2064 cm^{-1})	(S) Pellet surface area (cm^2)	A·S/m
0.0040	0.0522	0.0562	0.2758	0.773	0.785	10.80
0.0064	0.0587	0.0651	0.3810	1.171	0.785	14.12
0.0099	0.0542	0.0641	0.5985	2.235	0.785	27.37
0.0122	0.0592	0.0714	0.6622	3.311	0.785	36.40

**Figure R1.** (a) IR peak of CO corresponding to different amount $\text{Rh}(\text{CO})_2(\text{acac})$ mixed KBr samples, (b) correlation of Rh^+ molar concentration and IR $\text{Rh}^+(\text{CO})_2$ intensity.

In the case of Rh^{3+} , there are no commercial salts containing CO ligands which can be used as reference, which complicates the analysis of extinction coefficients.

In our previously publication², we reported a low-temperature IR-CO protocol for the identification of Rh^{3+} species, involving sample evacuation at 80 °C followed by CO titration at low temperature of -60 °C. Rh^{3+} has a weak interaction with CO and is easily reduced to Rh^+ at increasing CO coverages. Therefore to operate at low temperature is mandatory for a realistic quantification of Rh^{3+} species.

Two KRh@MFI calcined samples with different Rh loadings were prepared: 0.05 KRh@MFI-Cal (0.05wt% Rh), and 0.2 KRh@MFI-Cal (0.2wt% Rh). Considering that the Rh clusters size is approximately 0.4 nm, corresponding to about 2-3 Rh atoms, the Rh dispersion is close to 100%, and all Rh atoms are accessible to CO.

The IR spectra were acquired at $-60\text{ }^{\circ}\text{C}$ at increasing CO coverage (from 0.16 to 10 mbar) until saturation. At this condition, we assume that all Rh species are interacting with CO, and from curve-fitting of the IR spectra we can determine the peak area of the IR band corresponding to Rh^{3+} at 2137 cm^{-1} (see Figure R2)². Due to the coexistence of a small peak at 2120 cm^{-1} attributed to Rh^{2+} , we have considered both peak areas to define the adsorption coefficient of oxidise Rh^{n+} species (See Figure R2c and R2d). The inclusion or not of the peak area of Rh^{2+} , results in final errors of $\pm 30\%$ when calculating the $\text{Rh}^{3+}/\text{Rh}^{+}$ ratio.

The corresponding data are included in Table R2 and R3 and plotted in Figure R2.

Table R2. Calculation of Rh^{3+} extinction coefficient based on KRh@MFI-Cal .

Samples	Rh loading (wt%)	(m) Pellet weight (g)	(S) Pellet surface area (cm^2)	Overtone area	Rh concentration ($\times 10^{-3}\text{ mol/g}$)	(A) Rh^{3+} peak area ($\times 10^{-3}$)	A·S/m normalized to overtone ^a
0.05KRh@MFI-Cal	0.05	0.0163	0.785	50.53	0.486	7.91	0.00754
0.2KRh@MFI-Cal	0.20	0.0089	0.785	30.08	1.943	8.13	0.0238

^a The A·S/m values were normalized using the SiO_2 overtone band to compensate for variations in sample thickness and IR optical path caused by the heterogeneous nature of powder samples, thereby allowing a more reliable comparison between Rh concentration and peak area.

Table R3. Calculation of Rh^{3+} & Rh^{2+} extinction coefficient based on KRh@MFI-Cal .

Samples	Rh loading (wt%)	(m) Pellet weight (g)	(S) Pellet surface area (cm^2)	Overtone area	Rh concentration ($\times 10^{-3}\text{ mol/g}$)	(A) Rh^{3+} & Rh^{2+} peak area ($\times 10^{-3}$)	A·S/m normalized to overtone ^a
0.05KRh@MFI-Cal	0.05	0.0163	0.785	50.53	0.486	10.53	0.0100
0.2KRh@MFI-Cal	0.20	0.0089	0.785	30.08	1.943	10.94	0.0321

^a The A·S/m values were normalized using the SiO_2 overtone band to compensate for variations in sample thickness and IR optical path caused by the heterogeneous nature of powder samples, thereby allowing a more reliable comparison between Rh concentration and peak area.

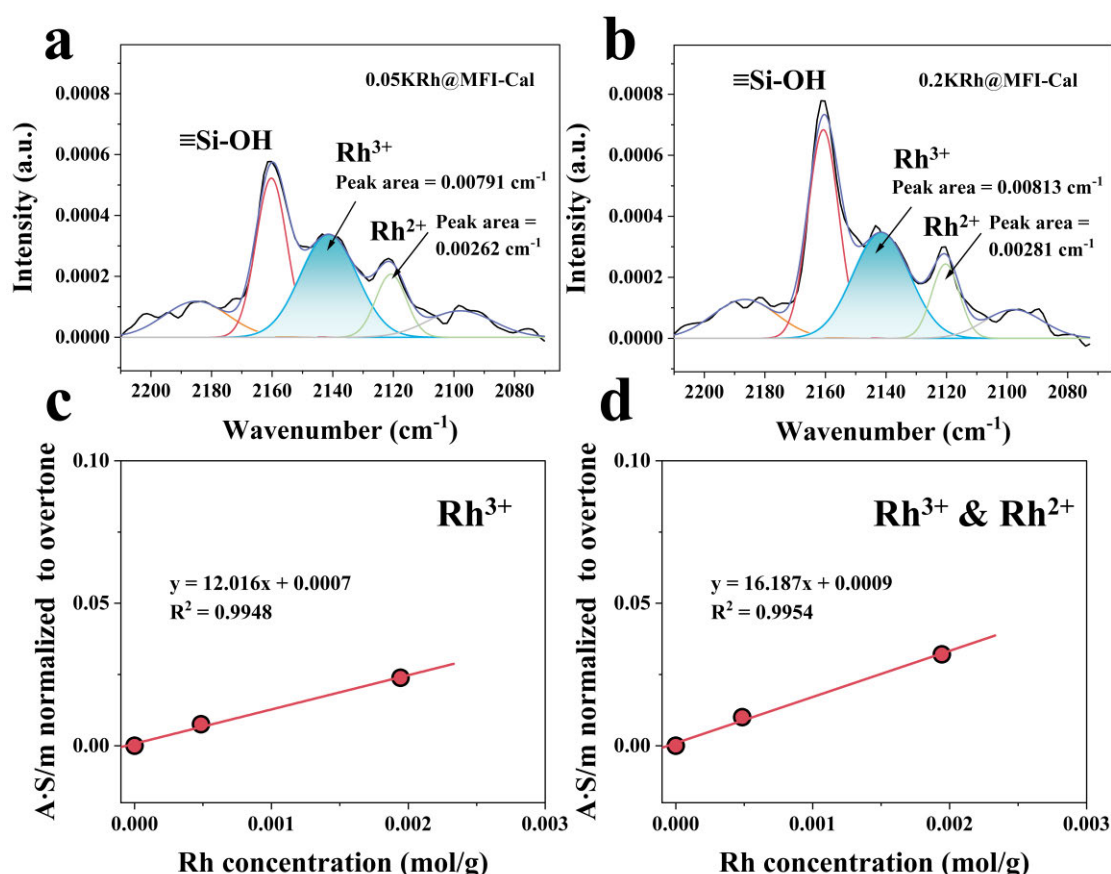


Figure R2. (a) Deconvolution of Rh³⁺ and Rh²⁺ species on 0.05KRh@MFI-Cal sample, (b) deconvolution of Rh³⁺ and Rh²⁺ species on 0.2KRh@MFI-Cal sample, (c) correlation Rh concentration and IR normalized Rh³⁺ integrated area. (d) correlation Rh concentration and IR normalized Rh³⁺ plus Rh²⁺ integrated areas.

Based on the above correlations, it is clear that at the same Rh concentration, the peak intensity for Rh⁺(CO)₂ is higher than that for Rh³⁺(CO). This is reasonable considering the different electronic configuration of both Rh³⁺ and Rh⁺ species. Indeed, Rh⁺ has a d⁸ electronic configuration, which enables strong π backdonation to adsorbed CO molecules. Electrons from the Rh d orbitals are donated into the π^* antibonding orbitals of CO, significantly altering the dipole moment of the C-O bond and resulting in extremely high infrared absorption intensity. Consequently, even at very low concentrations, the characteristic of Rh⁺(CO)₂ doublet is easily detected in IR spectrum.

In contrast, Rh³⁺ exhibits a d⁶ electronic structure with a higher positive charge and much stronger electron binding ability, which largely suppresses π -backdonation to CO. As a result, CO adsorption on Rh³⁺ is dominated by σ -donation from CO to the metal

center. In this case, the variation in dipole moment during C-O vibration is low, leading to weak IR absorption intensity of Rh^{3+} carbonyl species.

DFT calculated vibrational frequencies and CO intensity stretching frequencies of Rh^+ and Rh^{3+} species interacting with CO, reveals a lower intensity for Rh^{3+} than for Rh^+ (see Figure R3), in the direction of the IR results.

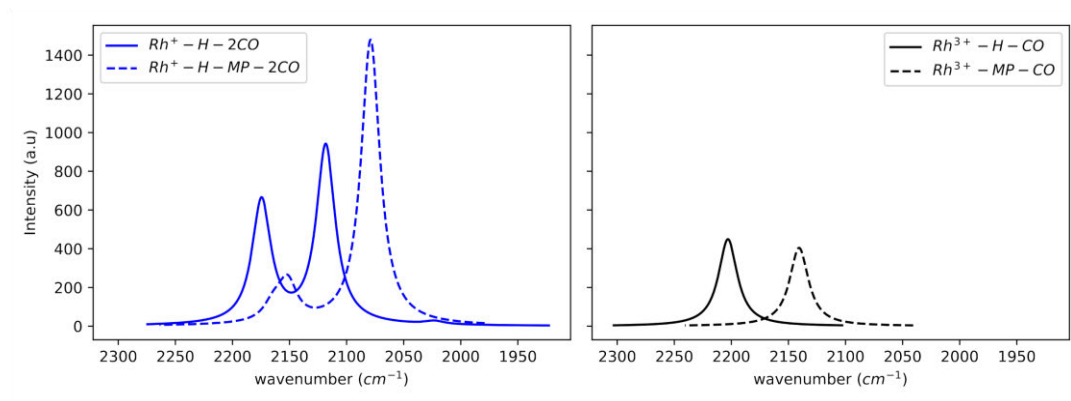


Figure R3. Calculated IR spectra for the optimized geometries of Rh^+ and Rh^{3+} included in **Table S7**. The shape of the peaks was calculated using a Lorentzian width of 20 cm^{-1} .

With these results in hand, we have estimated the relative amount of Rh^{3+} versus Rh^+ in the $\text{KRh@MFI-Cal-Toluene-CO/H}_2$ and in others KRh@MFI-Cal catalysts included in our work in Figure R4. This is now summarized in Table R5 for referee purpose.

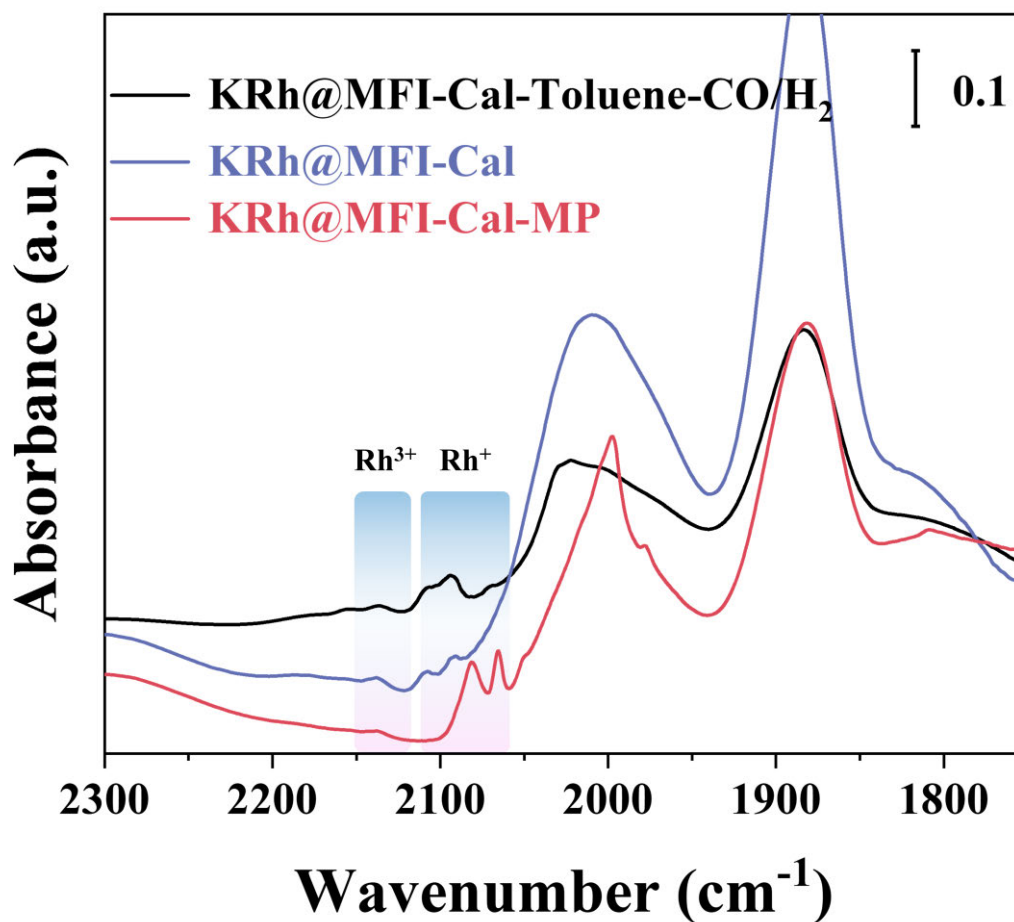


Figure R4. IR-CO at $-60\text{ }^{\circ}\text{C}$ and 2 mbar CO coverage spectra for KRh@MFI-Cal-Toluene-CO/H₂, KRh@MFI-Cal after 1-hexene hydroformylation reaction, and KRh@MFI-Cal-500MP after 1-hexene hydroformylation reaction.

Table R5. Rh³⁺, Rh⁺ concentrations in KRh@MFI-Cal catalysts system.

Samples	(m) Pellet weight (g)	(S) Pellet surface area (cm ²)	Overtone area	Rh ³⁺ peak area	Rh ⁺ peak intensity	Rh ³⁺ concentration ($\times 10^{-3}$ mol/g) ^a	Rh ⁺ concentration ($\times 10^{-5}$ mol/g)	Rh ³⁺ / Rh ⁺ molar ratio ^a
KRh@MFI-Cal	0.0192	0.785	103.69	0.07201	0.01138	1.7 - 2.3	5.4	31.2 - 42.4
KRh@MFI-Cal-MP	0.0161	0.785	43.363	0.03919	0.06153	2.7 - 3.6	10.3	26.0 - 35.1
KRh@MFI-Cal-Toluene-CO/H ₂	0.0146	0.785	41.072	0.08158	0.02547	6.5 - 8.8	7.2	91.3 - 123.3

^a The range was determined by taking the equations in Figure R2c and R2d into consideration.

We would like to admit that this calculation method involves uncertainties, primarily due to the lack of a well-defined Rh³⁺ reference system, the potential partial reduction

of Rh^{3+} under low-temperature CO titration conditions, the lack of accurate quantification of sites interacting with CO and the absence of a pure Rh^{3+} containing reference sample. Nevertheless, this approach still provides a useful semi-quantitative indication of the relative $\text{Rh}^{3+}/\text{Rh}^+$ molar ratio, offering insight into the predominant Rh species distribution. This IR-CO quantification clearly confirms that Rh^{3+} species are the predominant Rh form in the KRh@MFI-Cal-Toluene-CO/ H_2 sample.

A discussion on semi-quantitative assessment of the $\text{Rh}^{3+}/\text{Rh}^+$ ratio has been now included in the new version of the Supporting Information, in Appendix 4.3. In the text we have slightly modified the paragraph: “the KRh@MFI-Cal sample has been pretreated at 40 bar CO/ H_2 in toluene for 2h (labelled as KRh@MFI-Cal-Toluene-CO/ H_2 sample) resulting in the disruption of the initial Rh_2O_3 cluster with the formation of predominant Rh^{3+} , in coexistence with some Rh^+ , based on semi-quantitative IR-CO data (Figure S17)”.

2) Furthermore, for the KRh@MFI-Cal-Toluene-CO/ H_2 sample, only CO-FTIR characterization is presented. Additional complementary techniques (e.g., XAS, H_2 -TPR) would be highly valuable to corroborate the proposed oxidation state and coordination environment of Rh species.

Response: We thank the referee meaningful comment.

As we discussed in Question 1, the $\text{Rh}^{3+}/\text{Rh}^+$ molar ratio is 91.3 - 123.3 based on IR-CO quantification method, despite the inherent uncertainties associated with this approach.

On the other hand, and in agreement with the referee we have deeply investigated the quantification of Rh sites based on the XANES spectra. Unfortunately, by XAS it is not possible in the present case, because of the limited reference data sets. Indeed, CO ligands is expected to greatly affect the Density of State of Rh and this could bring to misinterpretations of the XANES spectra^{3,4}. An attempt of quantification by Multivariate Curve Resolution Analysis (MCR) analysis is reported in the reply to

referee 2. Comparing the obtained results with the IR data, it seems that the MCR 3rd component corresponds to overlapping Rh^+ and Rh^{3+} contributions, limiting a direct quantification.

We already commented in the original version of the manuscript about the uncertainty of XAS analysis for quantitative $\text{Rh}^{3+}/\text{Rh}^+$ analysis. In the new version of the manuscript, we have added a more detailed discussion in Appendix 4.4 of Supporting Information: “However, the linear combination fitting (LCF) and Multivariate Curve Resolution Analysis (MCR) with the reference spectra did not allow an accurate quantitative determination of both Rh^{3+} and Rh^+ species in the spent sample (More discussions in Appendix 4.4 of Supporting Information)”.

3) A related concern arises from the intrinsic reaction rate (R_0) for isomerization. The Rh^{3+} -enriched sample ($\text{KRh@MFI-Cal-Toluene-CO/H}_2$) exhibits an R_0 that is approximately two orders of magnitude lower than that of the Rh^+ -rich sample (KRh@MFI-CalRed-CO).

I wonder how would the activity and linear-to-branched (l/b) ratio evolve upon additive incorporation in the Rh^{3+} system? Such comparisons could help clarify whether the additive effect is specific to Rh^+ sites or more general.

Response: We thank the reviewer for the comment.

We suspect that the referee has been confused in identifying the $\text{KRh@MFI-CalRed-CO-MP}$ (Violet-blue line) as $\text{KRh@MFI-Cal-Toluene-CO/H}_2$ sample (Blue line). As shown in Figure S16 of the SI (Figure R5 for referee), the isomerization rate of KRh@MFI-CalRed-CO sample (Red line) is approximately two orders of magnitude higher than that of the same catalyst in the presence of MP additive, and in both cases higher than that of the $\text{KRh@MFI-Cal-Toluene-CO/H}_2$ sample, in which Rh^{3+} species are predominant. In this sample the 1-hexene isomerization rate is close to zero (0.17×10^{-3} mmol/h), and further decrease by a factor of ~20% upon addition of the MP additive.

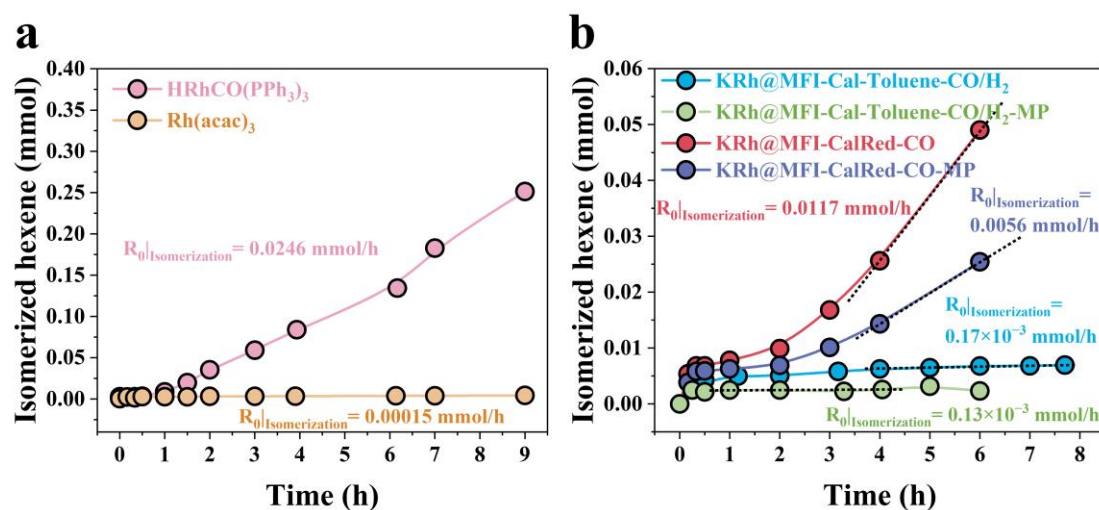


Figure R5. Time profiles of 1-hexene isomerization activity of 1-hexene isomerization activity on (a) homogeneous $\text{RhHCO}(\text{PPh}_3)_3$ and $\text{Rh}(\text{acac})_3$ catalysts, (b) heterogeneous $\text{KRh@MFI-Cal-Toluene-CO}/\text{H}_2$, $\text{KRh@MFI-Cal-Toluene-CO}/\text{H}_2\text{-MP}$, KRh@MFI-CalRed-CO and $\text{KRh@MFI-CalRed-CO-500MP}$ catalysts at 40 bar N_2 . Reaction condition: Isomerization: 1 mmol LAO, 20 mg catalyst (0.00038 mmol Rh), 20 mg decane (internal standard), 4 mL toluene, 40 bar N_2 , 80 °C, 800 rpm.

We have updated this information in section 2.8 of Supporting Information.

4) More generally, the conclusions regarding the distinct roles of Rh^{3+} and Rh^+ species in governing l/b ratio are compared in MFI zeolite. Was this conclusion also can be applied in to some other topologies like FAU or FER.

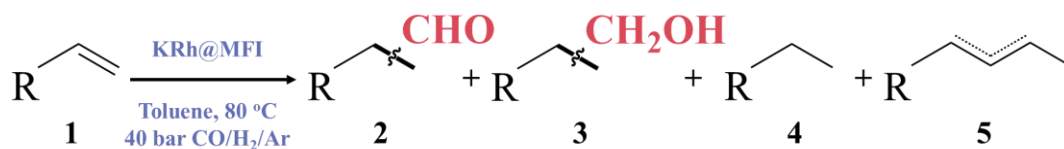
Response:

Following the referee's recommendation, we prepared Rh@Na-FER and Rh@Na-FAU zeolites following the one-pot synthesis approach⁵. Metal loadings are close to that of the KRh@MFI-Cal sample of our work (see Table R7). In addition, both samples show good crystallinity based on the XRD pattern and STEM images (Figure R7 and Figure R8, respectively).

The catalytic data in 1-decene hydroformylation are given in Figure R6a-d and summarized in Table R6. As expected, due to the acidity of these samples, the yields of isomerized olefins are higher than that of aldehydes, resulting in significantly lower aldehydes l/b ratios. However, similar to our work, in the presence of NMP additive,

both, isomerization and hydroformylation rates are significantly suppressed (Table R6 and Figure R6e and R6f), indicating that NMP can coordinate with both $\equiv\text{Si-O(H)-Al}$ acid sites and Rh^+ species.

Table R6. Catalytic results for KRh@MFI-Cal , Rh@Na-FER-Cal , and Rh@Na-FAU-Cal catalysts of 1-decene hydroformylation at 80 °C.^a



Entry	Catalysts	Conv. (%)	Selec. (%) Aldehyde (L) ^b	l/b ^c	Yield (%)				R_0 (mmol/h) ^d L-Aldehyde	R_0 (mmol/h) ^d Iso-Alkenes	TON ^e	TOF (h ⁻¹) ^f
					2	3	4	5				
1	KRh@MFI-Cal	99.4	92.1 (89.2)	30	91.6	0	1.2	6.6	0.85	0.036	2137	2096
2	KRh@MFI-Cal-500MP	98.5	96.8 (96.5)	378	95.3	0	0.5	2.6	0.82	0.018	2279	2052
4 ^g	$\text{KRh@MFI-Cal-4000NMP}$	99.8	95.9 (95.8)	817	95.7	0	1.0	3.1	0.67	0.017	2406	1706
5 ^h	Rh@Na-FER-Cal	74.5	57.2 (39.3)	2.2	42.6	0	0.2	31.7	0.02	0.040	1543	87
6 ⁱ	Rh@Na-FAU-Cal	99.3	63.6 (38.2)	1.5	63.1	0	1.5	34.7	0.08	0.117	1523	310
7 ^j	$\text{Rh@Na-FAU-Cal-4000NMP}$	15.4	50.6 (40.9)	4.3	7.8	0	0.2	7.4	0.01	0.008	321	22

^a Reaction conditions: 1 mmol LAO, 20 mg catalyst (0.00038 mmol Rh), 20 mg isooctane (internal standard), 4 mL toluene, 40 bar $\text{CO/H}_2/\text{Ar}$ (45/45/10 vol%), 80 °C, 800 rpm and 3h reaction.

^b Total aldehyde selectivity (L=Linear aldehyde selectivity).

^c Ratio of the linear aldehyde to the branched aldehyde.

^d Reaction rate for linear aldehyde formation and reaction rate for isomerized alkenes formation, mmol/h, calculated when LAO conversion is < 20%.

^e mmol of linear aldehyde/total mmol of Rh at 3h reaction time.

^f Rate for the formation of linear aldehyde/total mmol of Rh.

^g 9h reaction.

^h 22h reaction.

ⁱ 7h reaction.

^j 22h reaction.

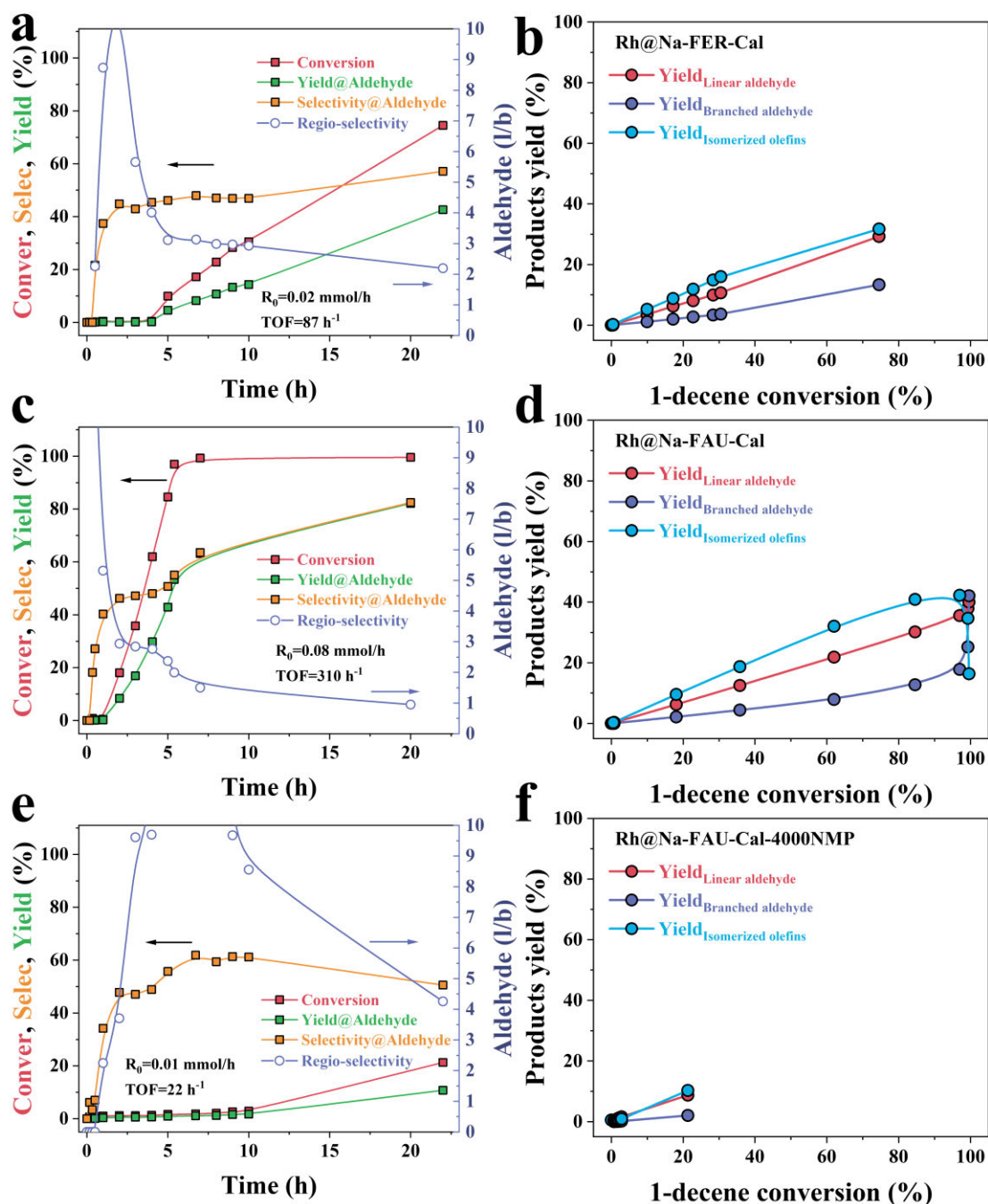


Figure R6. 1-Decene hydroformylation: (a) Time profiles of activity on Rh@Na-FER-Cal catalyst and (b) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (c) Time profiles of activity Rh@Na-FAU-Cal catalyst and (d) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (e) Time profiles of activity Rh@Na-FAU-Cal-4000NMP catalyst and (f) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. Reaction condition: 1 mmol LAO, 20 mg catalyst, 20 mg isooctane (internal standard), 4 mL toluene, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm, R_0 , TOF and TON are values for linear aldehyde formation.

Table R7. Physicochemical properties of Rh-based catalysts.

Catalysts	K (wt%) ^a	Na (wt%) ^a	Al (wt%) ^a	Si/Al molar ratio ^a	Rh (wt%) ^a
KRh@MFI-Cal	1.0	-	-	-	0.20
Rh@Na-FER-Cal	-	1.5	6.0	6.2	0.10
Rh@Na-FAU-Cal	-	10.6	10.4	3.0	0.13

^a Measured by ICP-OES analysis.

XRD:

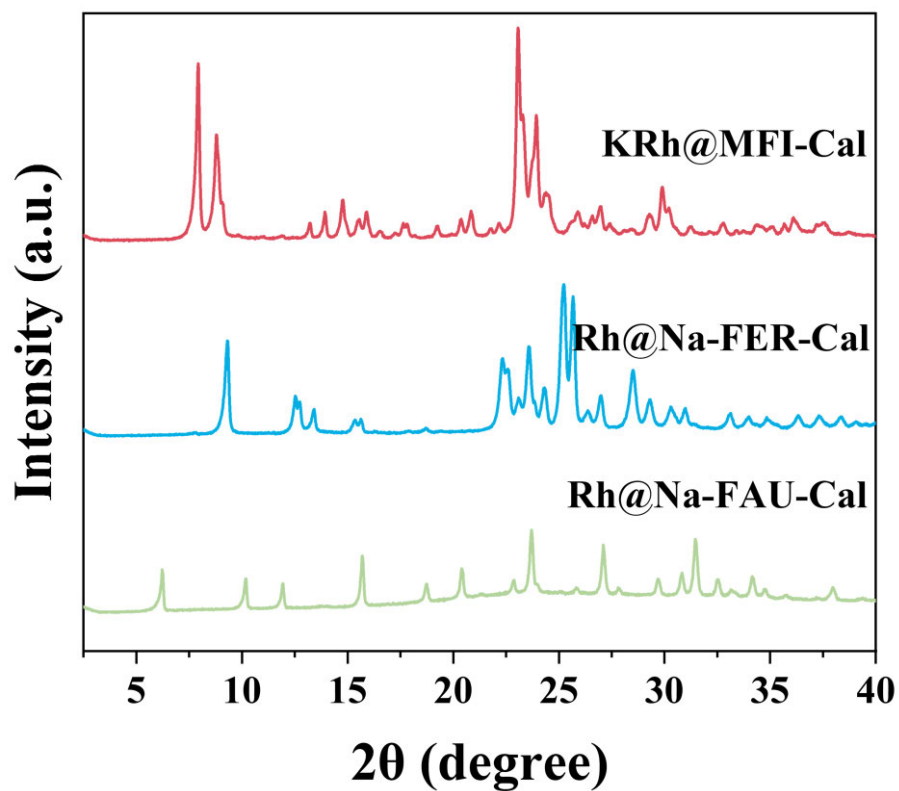


Figure R7. XRD of KRh@MFI-Cal, Rh@Na-FER-Cal and Rh@Na-FAU-Cal samples.

STEM:

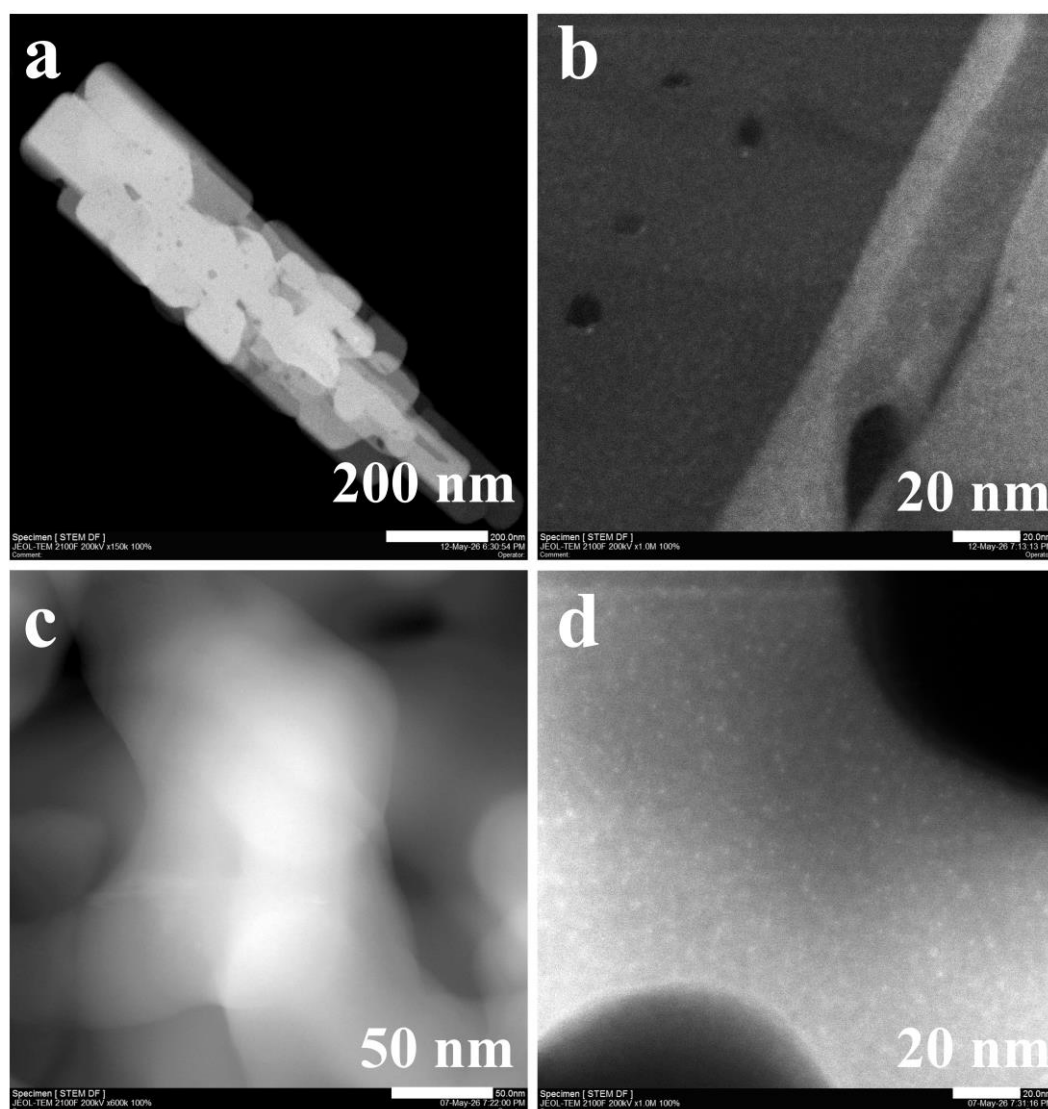


Figure R8. STEM images of (a, b) Rh@Na-FER-Cal, and (c, d) Rh@Na-FAU-Cal catalysts.

5) The authors report a significant increase in the linear-to-branched (l/b) ratio (from 20 up to 378 or higher) upon addition of organic additives, which is attributed to modification of the electronic properties of Rh^+ species. Ex situ IR spectra (Figure 2i, B and C) indeed show clear differences between catalysts used w/ and w/o MP.

To further substantiate this interpretation, it would be highly valuable to perform in situ CO-FTIR measurements under reaction-relevant conditions with gradual co-feeding of MP. If the proposed electronic modulation of Rh^+ is correct, one might expect a measurable shift (e.g., red shift) in the $\text{Rh}^+\text{--CO}$ stretching frequencies. Such data would

provide more direct evidence for the proposed mechanism.

Response: We thank the reviewer for the comment. To perform IR studies in liquid phase under high syngas pressure and by co-feeding MP (with characteristic IR bands at 1944, 1863, 1802, 1612, 1500, 719 cm^{-1}) is challenging, particularly when analyzing components in the $\text{C}\equiv\text{O}$ region. This is due to the overlap between the signals of syngas, MP and Rh carbonyl species, making difficult to resolve and analyze the Rh active sites involved in the hydroformylation reaction. Nevertheless, and to take into account the comment of the referee, we performed the following experiments:

We used the $\text{KRh@MFI-Toluene-Cal-CO/H}_2$ sample, which after low-temperature CO titration, shows both Rh^{3+} and $\text{Rh}^+(\text{CO})_2$ species (Figure R9). Subsequently, 1.7-2.4 mbar of MP was co-add into the IR cell. A red shift of the $\text{Rh}^+(\text{CO})_2$ bands from 2090 and 2011 cm^{-1} to 2081 and 2000 cm^{-1} was observed upon 2.4 mbar MP dosing, while the position of the Rh^{3+} peak remained unchanged (Figure R9), in line with that observed in our work.

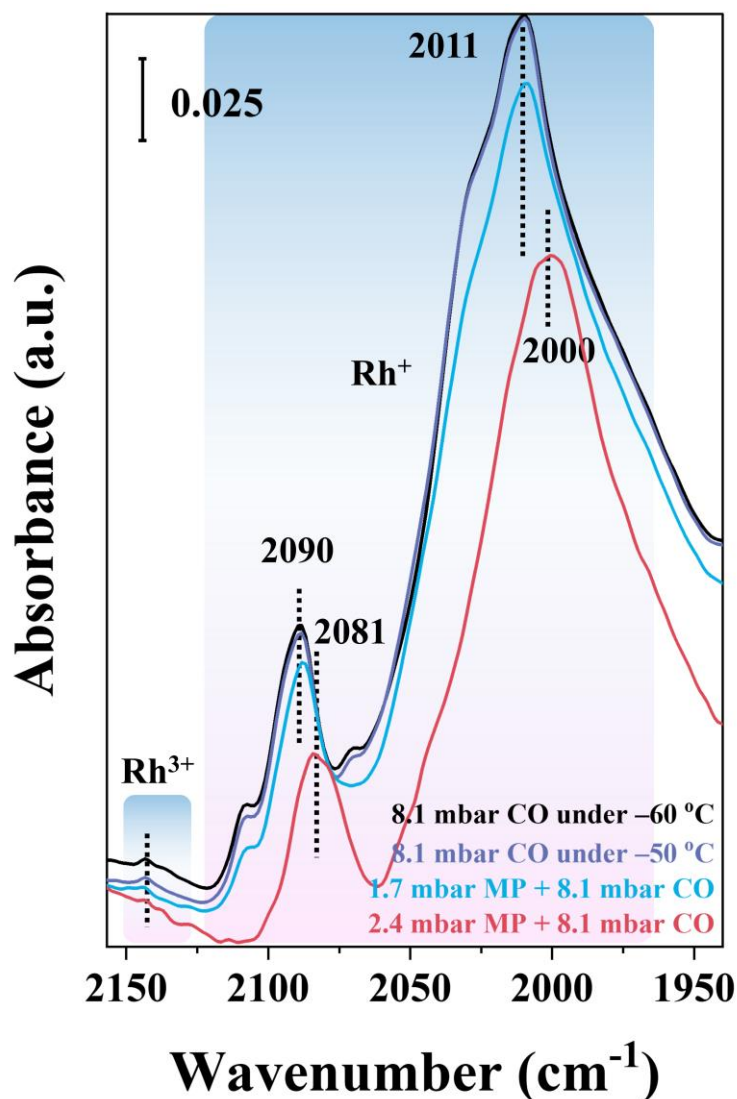


Figure R9. IR-CO of KRh@MFI-Cal-Toluene-CO/H₂ sample with MP titration.

We have updated this information in Supporting Information of section 2.14.

6) The optimization of the MP/Rh ratio (reported as 500) raises an additional question. As shown in Table S8, increasing the MP/Rh ratio leads to a decrease in catalytic rate. If MP primarily acts by selectively blocking or modifying Rh⁺ sites, one might expect the reaction rate to remain relatively constant beyond a certain threshold. However, the observed rate suppression therefore suggests that MP may also influence substrate accessibility, active site availability, or reaction kinetics in a more complex manner. The authors should explain more about this point. Also, it would be interesting to explore the extreme case where MP is used as the solvent. How would the catalytic activity and

l/b ratio behave under such conditions?

Response: We thank the reviewer for the valuable comments.

In response to the first comment of the reviewer “if MP primarily acts by selectively blocking or modifying Rh^+ sites, one might expect the reaction rate to remain relatively constant beyond a certain threshold”, we want to point out that although Rh^+ species are largely suppressed in the presence of MP inhibiting isomerization, they still contribute, to some extent, to the formation of linear aldehydes via hydroformylation activity (Figure 2c in the manuscript). This explains the decrease in catalytic rate by increasing the MP/Rh ratio.

On the other hand, as suggested by the reviewer, we performed additional 1-hexene, 1-octene and 1-decene hydroformylation experiments using MP and NMP as solvents. As shown in Figure R10a and R10b, significantly enhanced l/b ratios were obtained in the presence of either MP or NMP. An l/b ratio > 400 was achieved at $> 90\%$ 1-hexene conversion when MP was used as solvent, while exclusively linear aldehyde formation was observed in the presence of NMP. Also high l/b values were obtained for 1-octene hydroformylation (l/b > 400 at $> 90\%$ 1-octene conversion) and 1-decene hydroformylation (l/b > 600 at $> 90\%$ 1-decene conversion) (Figure R10c and R10d).

Notice that by increasing the amount of MP and NMP, the reaction rate gradually decreases and reaches a plateau with MP used as solvent. In contrast, the hydroformylation rate drops to a very low level in the presence of NMP as solvent. This difference is reasonable, as MP has a smaller molecular size than NMP and can more readily diffuse in and out of the MFI zeolite channels, whereas excessive NMP may hinder olefin accessibility within the zeolite channels.

Based on these results, we determined an optimal operating windows for MP and NMP respectively. The optima MP/Rh molar ratio is 500 until MP as solvent, whereas the optimal NMP/Rh molar ratio is approximately 3000-8000 (Figure R10e and R10f).

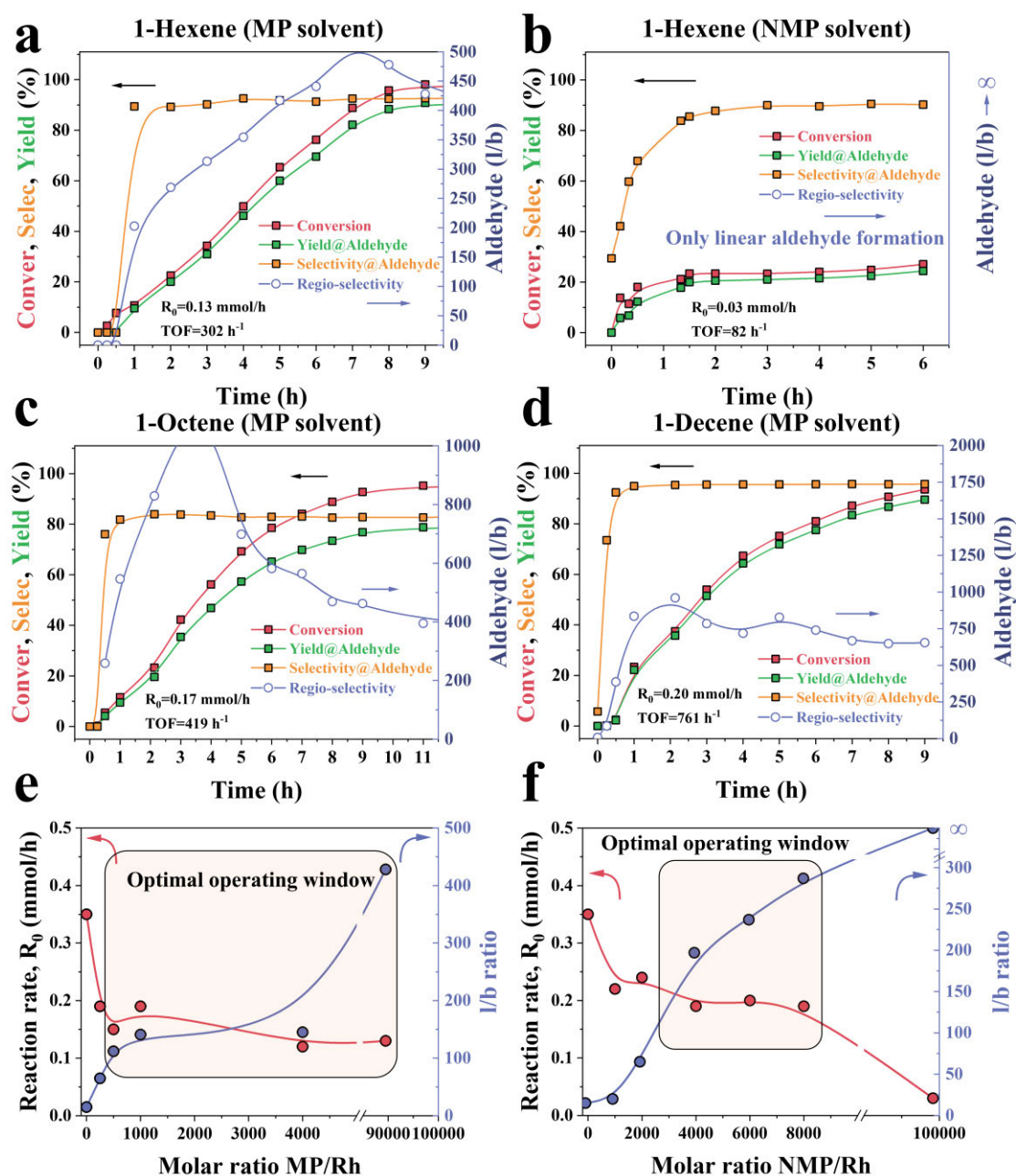


Figure R10. (a, b) 1-Hexene hydroformylation activity of KRh@MFI-Cal with MP as solvent (a), NMP as solvent (b), (c) 1-octene hydroformylation activity of KRh@MFI-Cal with MP as solvent, (d) 1-decene hydroformylation activity of KRh@MFI-Cal with MP as solvent, (e) correlation of linear aldehyde formation rate and I/b ratio with MP or NMP additive amount in 1-hexene hydroformylation. Reaction condition: 1 mmol LAO, 20 mg catalyst (0.00038 mmol Rh), 20 mg decane or isooctane (internal standard), 4 mL MP or NMP as solvent, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm, R_0 , TOF and TON are values for linear aldehyde formation.

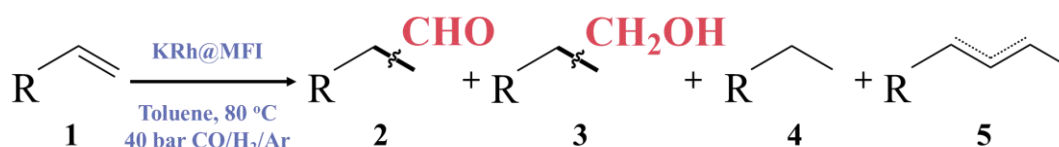
We have updated this result in the Supporting Information, section 2.21. Also we included a comment in the new version of the manuscript: “Furthermore, when operating under pure MP or NMP as solvents, the regioselectivity is further enhanced

at expense of a drop of activity (Figure S43)”.

7) For Table S8, when MP/Rh=4000 (entry 5). The reported aldehyde yield (54.1%) appears inconsistent with the product of the given conversion and selectivity (84.4% × 89.7%). The authors are requested to clarify this discrepancy and provide the calculation formulas in the Supporting Information.

Response: We thank the reviewer for the carefully check. Yes, we wrongly copied the data of entry 5 after 7h reaction result. It should be 84.4% 1-hexene conversion, 91.3% aldehydes (90.6% linear aldehyde) selectivity. We revised this information in Table S8.

Table R8. Catalytic results for KRh@MFI catalyst of 1-hexene hydroformylation in the presence of N-Methylpyrrolidine.^a



Entry	Organic additive	Molar ratio to Rh	Conv. (%)	Selec. (%) Aldehyde (L) ^b	l/b ^c	Yield (%)				R ₀ (mmol/h) ^d L-Aldehyde	R ₀ (mmol/h) ^d Iso-Alkenes	TON ^e	TOF (h ⁻¹) ^f
						2	3	4	5				
1 ^g	/	/	99.5	90.9 (85.1)	15	90.4	0	1.1	8.0	0.35	0.050	2024	872
2	MP	250	93.8	90.0 (88.7)	65	84.4	0	1.2	8.1	0.19	0.014	2158	486
3	MP	500	99.6	92.8 (91.9)	112	92.4	0	1.5	5.7	0.15	0.010	2386	394
4 ^h	MP	1000	99.6	94.2 (93.6)	141	93.9	0	1.3	4.4	0.19	0.011	2364	482
5 ⁱ	MP	4000	84.4	91.3 (90.6)	145	77.0	0	1.1	6.3	0.12	0.010	1943	292
6 ^j	MP	Solvent	98.1	92.6 (92.4)	428	90.9	0	1.4	5.8	0.13	0.009	2216	302

^a Reaction conditions: 1 mmol LAO, 20 mg catalyst (0.00038 mmol Rh), 20 mg decane (internal standard), 4 mL toluene, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm and 5h reaction.

^b Total aldehyde selectivity (L=Linear aldehyde selectivity).

^c Ratio of the linear aldehyde to the branched aldehyde.

^d Reaction rate for linear aldehyde formation and reaction rate for isomerized alkenes formation, mmol/h, calculated when LAO conversion is < 20%.

^e mmol of linear aldehyde/total mmol of Rh at 5h reaction time.

^f Rate for the formation of linear aldehyde/total mmol of Rh.

^g 4h reaction.

^h 6h reaction.

ⁱ 7h reaction.

^j 9h reaction.

We have updated the calculation details in Method part of Manuscript:

The conversion, selectivity, yields, reaction rate (R_0), turnover numbers (TON) and turnover frequencies (TOF) were determined by the equations (1)-(8). The elemental balance of carbon was $100 \pm 5\%$. The TON and TOF were calculated using the number of Rh sites assuming that all Rh was atomically dispersed.

$$\text{Conversion } (X_{LAO}, \%) = \frac{n_0 (LAO) - n_i (LAO)}{n_0 (LAO)} * 100 \quad (1)$$

$$S_i (\%) = \frac{n_i}{n_{Isomers} + n_{Alkane} + n_{Aldehydes} + n_{Alcohols}} * 100 \quad (2)$$

$$l/b = \frac{n_{Linear \text{ aldehyde}}}{n_{Branched \text{ aldehyde}}} \quad (3)$$

$$\text{Yield } (Y_i, \%) = (X_{LAO} * S_i) / 100 \quad (4)$$

$$R_0 (i, mmol/h) = \left. \frac{d[n_i]}{dt} \right|_{t=0} \quad (5)$$

$$TON (i) = \frac{n_i * M_{Rh}}{m_{cat} * D_{Rh} * W_{Rh}} \quad (6)$$

$$TOF (i, h^{-1}) = \frac{R_0 (i) * M_{Rh}}{m_{cat} * D_{Rh} * W_{Rh}} \quad (7)$$

$$\text{Carbon balance } (\%) = \frac{\text{Total moles carbon in all products}}{\text{Total moles of carbon in initial reactants}} * 100 \quad (8)$$

Where n_i stands for the moles of i -compounds, $n_0 (LAO)$ is the initial moles of LAO. M_{Rh} is the molar mass of Rh, W_{Rh} is the loading weight of Rh, D_{Rh} is the dispersion of Rh, m_{cat} is the weight of catalyst used for reaction.

8) For the TON calculation, the number of Rh active sites should be reconsidered, as the MP blocks the Rh⁺ sites.

Response: We thank the reviewer for the comment.

As discussed in our response to Question 1, due to the inherent uncertainties in the accurate quantification of Rh³⁺ and Rh⁺ concentrations in the KRh@MFI-Cal catalytic it would be difficult to give reliable results for TON number based on exclusively Rh³⁺ species.

9) I recommend the author can test hydroformylation of cyclohexene and allylbenzene. What would the rates and l/b rate change w/ and w/o MP additives.

Response: We thank the reviewer for the meaningful comment.

As suggested by the referee, we investigated the hydroformylation of cyclohexene and *p*-methoxyallylbenzene over KRh@MFI-Cal catalyst. Allylbenzene was not available in our laboratory, and therefore we selected *p*-methoxyallylbenzene due to structural similarity to allylbenzene. Both substrates exhibited nearly ~0% activity over 11h reaction (Figure R11a). No Rh leaching was observed in both cases. The ~0% activity can be attributed to the relatively large kinetic diameter of cyclohexene (5.85-6.0 Å)^{6,7}, which is comparable to or exceeds the pore aperture of MFI zeolite channels (Figure R11b).

Even if partial diffusion into the MFI channels is possible due to zeolite framework flexibility, the subsequent C=C coordination to the Rh center preferentially located in the sinusoidal channels is still strongly hindered, as cyclohexene lacks sufficient conformational adaptability to properly align its double bond within the confined environment. Moreover, the corresponding hydroformylation product (cyclohexanecarboxaldehyde), bearing an additional aldehyde substituent and a rigid chair conformation, is unable to diffuse out of the MFI channels due to increased steric constraints.

A similar explanation can be applied to *p*-methoxyallylbenzene and other bulky cyclic

substrates with large kinetic diameters.

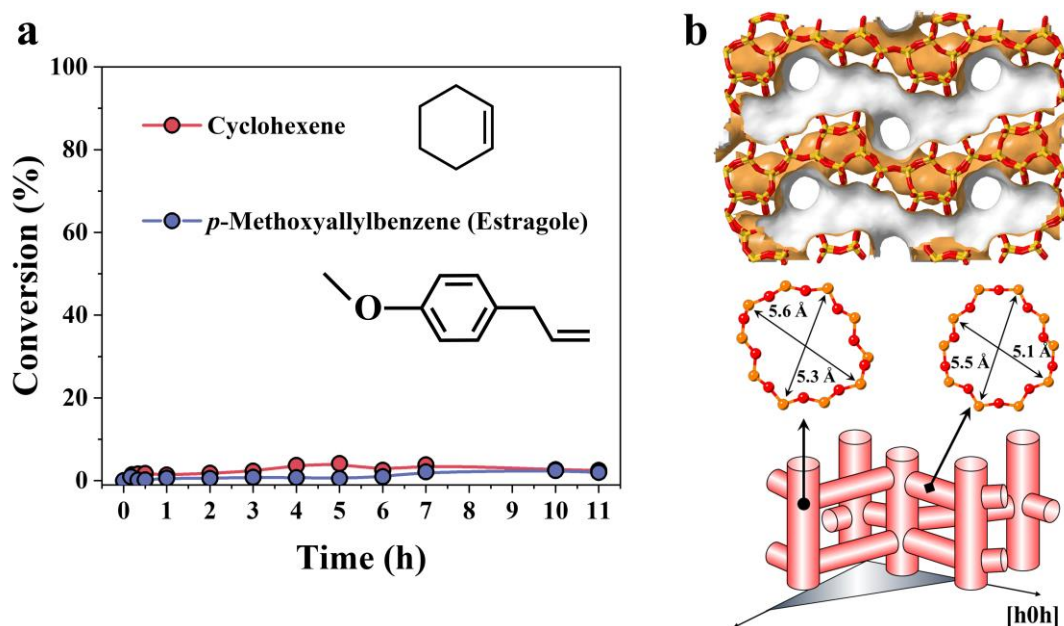


Figure R11. (a) Cyclohexene and *p*-methoxyallylbenzene hydroformylation on KRh@MFI-Cal catalyst, (b) illustration of MFI zeolite channel and corresponding straight channel size and sinusoidal channel size.

10) Minor points. Some figures in SI were not mentioned in manuscript like Figure S1, S39. The authors should either reference these figures where relevant or remove them if they do not contribute to the key conclusions.

Response: We thank the reviewer for the meaningful comment. We have updated some of the relevant Figures in the Manuscript. However, due to space and word-count limitations, we have removed a substantial amount of nonessential discussion to make the manuscript more compact. Furthermore, the figures included in the Supporting Information are crucial for supporting the conclusions of this work. Therefore, we decided not to remove those that are not explicitly discussed in the main text. Nevertheless, detailed annotations have been added to the Supporting Information to help readers better understand the context and significance of the data.

Referee #2

Comments:

The manuscript of Zhao et al describes the synthesis of Rh-based heterogenous hydroformylation catalysts based on Rh(III) sites stabilized in the sinusoidal medium pores of an MFI zeolite. This catalyst shows unprecedented activity and linear/branched selectivity and it is proposed in particular that Rh(III) is the desired active sites, while Rh(I) promotes olefin isomerization. It is also demonstrated that adding an organic additive like N-methylpyrrolidine greatly enhanced the selectivity by poisoning the Rh(I) sites. The work is certainly impactful and demonstrate a major advance in the field. Nonetheless several key questions need to be addressed before being published in Nature.

Response: We sincerely thank the reviewer for the positive and constructive evaluation of our work.

1) The nature of the surface sites remain difficult to understand; using more molecular reference compounds with and without CO ligands would likely help deciphering the structure of the surface sites. Note that one has to be careful in choosing references because CO ligands greatly affect the Density of State of Rh and may thus not be adequate to understand “oxidation state” of sites without carbonyl (comparing Rh(I)CO complex with Rh(III) acac can potentially lead to misinterpretation of the XANES spectra.

Response: We thanks the reviewer for this comment and we fully agree with the concern raised. We are aware that the selected references do not necessarily represent the investigated samples. The complete reference database considered in the analysis did not sufficiently cover the effect of the CO ligand and included only Rh₂O₃, Rh(CO)₂(acac), and Rh foil, RhCl₃, dimer Rh₂(OAc)₄ and Rh(ac)(C₂H₄)₂ (Figure R12).

As originally discussed, Rh₂O₃, Rh(CO)₂(acac), and Rh foil have been identified as the most close references to represent the data set. In particular, the FT of the k^2 weighted

EXAFS oscillations was suggesting a high fraction of CO ligand contribution in the samples, but its effect on the XANES region was not discussed.

As correctly addressed by the referee to quantify the Rh oxidation state based on the XAS spectra can be challenging in the present case. Both linear combinations fitting (LCF) and Multivariate Curve Resolution Analysis (MCR) were attempted (Table R9 and R10). While similar trends are obtained by LCF and MCR, the MCR analysis allowed a better reconstruction of the sample spectra (Table R10). Indeed, the LCF, even if it allows to represent the already discussed trends, it did not satisfactorily reproduce the experimental spectral features, indicating that the available reference dataset is not fully representative of the local environments present in the samples. Indeed, the quantitative estimation of the $\text{Rh}^{3+}/\text{Rh}^+$ ratio which can be extracted do not agree with the data obtained by CO-FTIR.

The MCR approach was confirming the closeness of the main three components expected in the dataset, allowing at the same time to slightly variate them. Such flexibility is not possible within an LCF approach. The analysis converged in two components exactly overlapping with Rh metal (Rh^0) and Rh_2O_3 (Rh^{3+}) reference spectra, and a third component which slightly differs from $\text{Rh}(\text{CO})_2(\text{acac})$. Such contribution seems to corresponds to $\text{Rh}^{\delta+}$ oxidation state, with a local structure similar to the one of the $\text{Rh}(\text{CO})_2(\text{acac})$ reference and a slightly different electronic distribution. The quantitative results obtained by these two approaches are reported in Table R9 and R10.

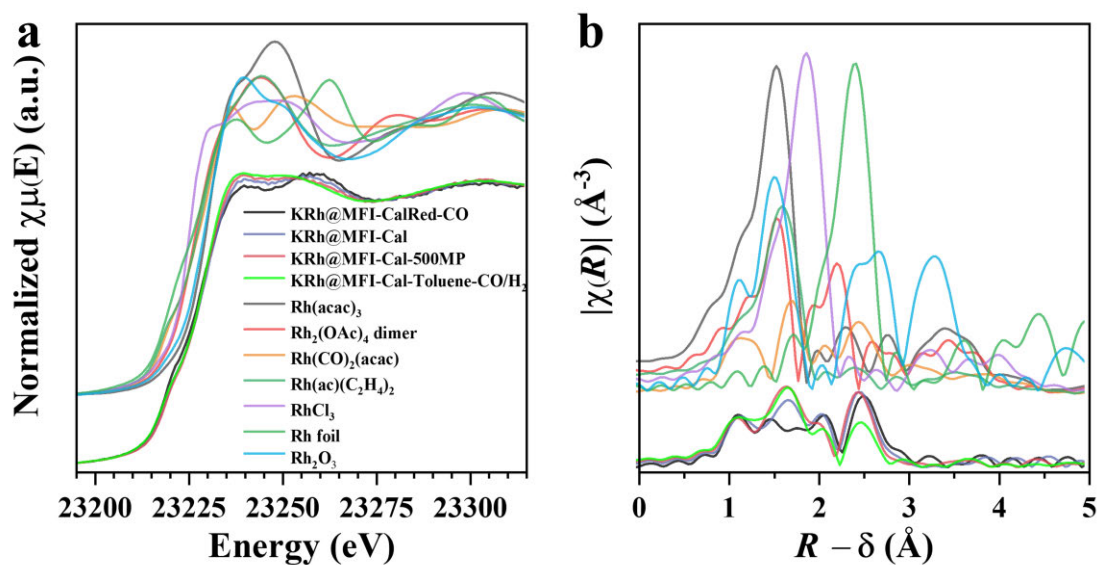


Figure R12. (a) Normalized XANES spectra and (b) k^2 -weighted FT of the EXAFS oscillations of catalysts compared with the full references data set. The FT of Rh foil was scale down by factor 2 for better representation.

Table R9. Results of the Athena-based LCF using Rh₂O₃, Rh(CO)₂(acac), and Rh foil as references. The analysis was carried out over an energy range from -70 to +130 eV.

Sample	Rh ⁰ weight	Rh ⁺ weight	Rh ³⁺ weight	R-factor
KRh@MFI-CalRed-CO	0.355 (0.043)	0.557 (0.039)	0.088 (0.019)	0.0012
KRh@MFI-Cal	0.252 (0.038)	0.541 (0.034)	0.207 (0.017)	0.0009
KRh@MFI-Cal-500MP	0.208 (0.032)	0.536 (0.029)	0.255 (0.014)	0.0006
KRh@MFI-Cal-Toluene-CO/H ₂	0.171 (0.038)	0.577 (0.034)	0.252 (0.017)	0.0009

Table R10. Results of the MCR analysis performed in ProQEXAFS⁸. The analysis was carried out over an energy range from –70 to +130 eV.

Sample	Rh ⁰ weight	Rh ^{δ+} weight	Rh ³⁺ weight	LOF, %*
KRh@MFI-CalRed-CO	0.343	0.657	0.0	0.33
KRh@MFI-Cal	0.283	0.566	0.151	0.07
KRh@MFI-Cal-500MP	0.232	0.571	0.196	0.35
KRh@MFI-Cal-Toluene-CO/H ₂	0.169	0.649	0.182	0.61

*The error metric is provided as lack of fit (LOF).

While similar trends are obtained from both LCF and MCR analyses, the MCR allowed a better reconstruction of the sample spectra. Figure R13a compares the reference spectra with the obtained MCR components, where the difference between the third component and Rh(CO)₂(acac) standard spectrum are highlighted by dashed lines. The catalyst KRh@MFI-CalRed-CO spectrum can now be satisfactorily reconstructed without requiring any Rh³⁺ contribution, in agreement with the IR data. To quantify the average Rh oxidation state would imply to know the oxidation state corresponding to the MCR 3rd component spectrum. Comparing the here reported results with the IR spectra it seems that the MCR 3rd component corresponds to overlapping Rh⁺ and Rh³⁺ contributions.

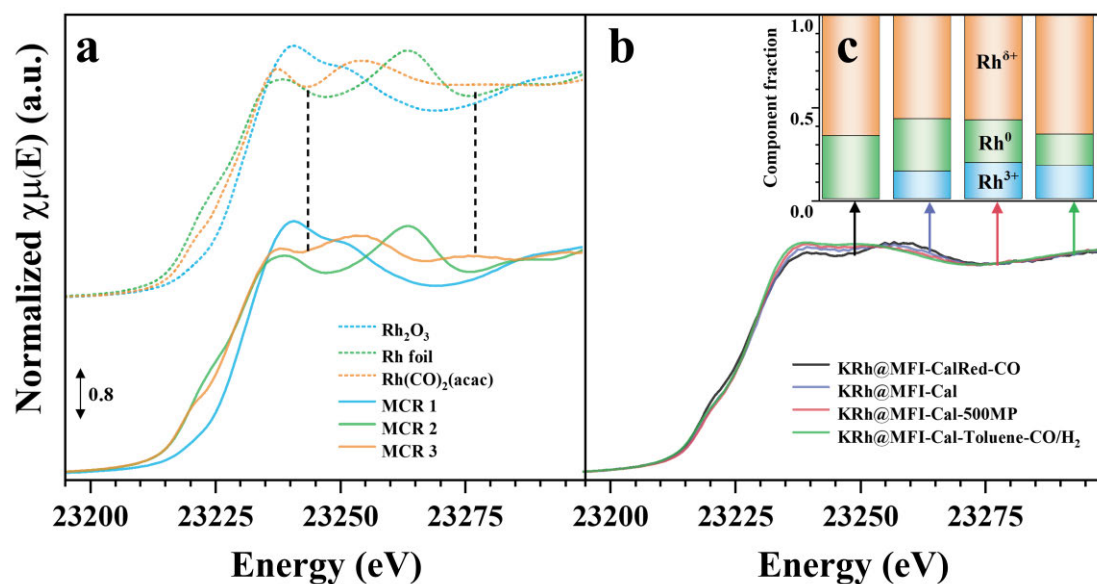


Figure R13. (a) MCR components (solid) and the corresponding reference XANES spectra (dotted). (b) Normalized XANES spectra of the samples. (c) MCR component concentration fraction (the color code is consistent across panels a, b, and c). The arrows indicate the correspondence between the spectra and their respective concentration profiles.

We have included a comment in the revised Supporting Information in Appendix 4.4, to highlight this effect.

2) The authors evaluate the hydroformylation mechanism via DFT calculations on simple models; however in the current manuscript, little space is being used to describe this model and the actual mechanism; the Reviewer argues that it is quite important because Rh(III) have been rarely proposed as active sites, hence the need to discuss the reaction mechanism. For instance, RhH intermediates are generated from RhCOR species, should it take place via oxidative addition or sigma-bond metathesis. In their mechanistic studies, they try to highlight the difference of isomerization properties of Rh(I) and Rh(III) but two very different species are used; Rh(I) with and Rh(III) one without hydride ligands; one could argue that not having hydride ligand helps to avoid isomerization. Yet, making Rh-Alkyl should involve the insertion of the olefins into a Rh-H. Overall, the reaction mechanism should be discussed in greater details. The authors could also use their model to probe the XANES as they did for the CO IR

signatures to better relate experiments and DFT modelling. Another important points: regarding the potential energy surfaces; they are provided in energies, ΔE ; the authors should provide the numbers in ΔH and ΔG . While only ΔG can be problematic giving both give a good view to the reader on how pertinent in the mechanism, while ΔE alone can be quite misleading (it often underestimates barriers).

Response: We thank the reviewer for this important comment and for emphasizing the need for a more detailed and rigorous discussion of the hydroformylation mechanism, particularly in the context of the less commonly proposed Rh(III) active sites. We have revised the manuscript to address these points.

First, we have expanded the description of the computational models and catalytic cycles in the Supporting Information (Section 2.11). In the revised version, we explicitly clarify that both Rh(I) and Rh(III) catalytic cycles involve hydride-containing intermediates, ensuring a more consistent comparison between the two oxidation states. This point was previously not sufficiently emphasized and is now clearly stated. For the Rh(I) cycle, the formation of Rh-H species from Rh-COR intermediates is described via the classical sequence involving oxidative addition of H_2 followed by reductive elimination steps, in agreement with the well-established hydroformylation mechanism. In contrast, for the Rh(III) system, we clarify that the regeneration of the Rh(III)-H species proceeds via a σ -bond metathesis pathway. Importantly, this mechanism allows the rhodium center to remain in the +3 oxidation state throughout the catalytic cycle, avoiding changes in formal oxidation state. This distinction between oxidative addition/reductive elimination (Rh(I)) and σ -bond metathesis (Rh(III)) pathways is now explicitly discussed in the revised Supporting Information.

Regarding the comparison of isomerization tendencies between Rh(I) and Rh(III), the reduced isomerization activity observed for the Rh(III) system is not due to the absence of hydride ligands, as both catalytic cycles do involve Rh-H intermediates. Instead, our calculations indicate that the suppression of isomerization in the Rh(III) pathway arises from a combination of a less favorable competition with CO coordination and a

significantly higher transition-state barrier associated with double-bond migration. This is included in the discussion of Figure 3 and in the Supporting Information of section 2.11.

We also fully agree with the reviewer regarding the importance of using thermodynamic quantities beyond electronic energies. In the revised manuscript, we have replaced the previously reported ΔE values with enthalpies (ΔH) and Gibbs free energies (ΔG) throughout. These values are now consistently reported in the main figures (Figure 3), in the Supporting Information (Figure S24), and in the corresponding Tables (Table S5). This provides a more realistic description of reaction energetics, particularly for activation barriers, and allows for a more reliable assessment of the catalytic relevance of the proposed pathways.

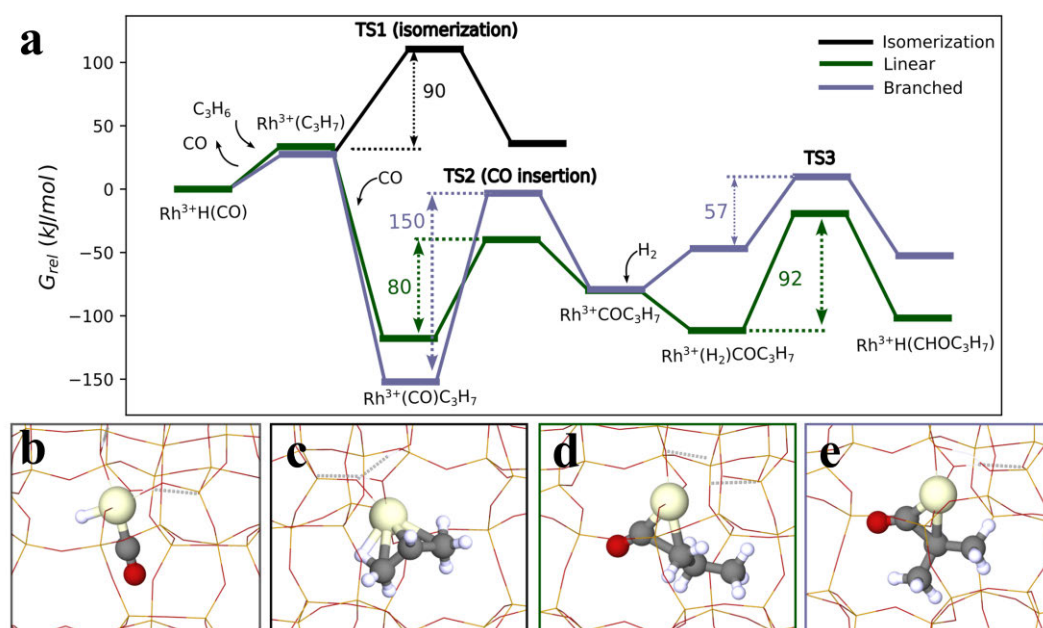


Figure 3. (a) Calculated free energy profile for hydroformylation and isomerization on a Rh^{3+} single-site center embedded in the MFI zeolite model, highlighting the key elementary steps along the catalytic cycle. Free energies were calculated at 77 °C. Optimized geometries of relevant states are shown. (b) initial octahedral $\text{Rh}^{3+}\text{-H(CO)}$ intermediate. (c) TS1 showing H transfer from C3 to Rh, leading to isomerized alkene. TS2 leading to propionyl intermediate along the (d) linear and (e) branched pathways, illustrating the structural features associated with the rate-determining step of the reaction pathway. O, Rh, C, Si and H atoms are shown in red, light yellow, grey, orange and white. MFI framework is represented with lines.

We revised the Supporting Information of section “2.11.4 Mechanism on MFI” as:

Having established that the mechanism is kinetically feasible for Rh^{3+} , we extended our study to the hydroformylation reaction on an MFI periodic model, to account for the local environment of $\text{Rh}^+/\text{Rh}^{3+}$ cations within a zeolite framework.

The active sites are modelled as $\text{Z-Rh}^+-\text{H}^-$ and $\text{Z-Rh}^{3+}-\text{H}^-$ species, i.e., a zeolite-bound Rh^+ and Rh^{3+} center charge-compensated by one hydride ligand and (for Rh^{3+}) two negatively charged siloxy groups (Figure S26). Up to acyl formation, the reaction mechanisms are, involving competitive propene adsorption, hydride-driven propyl formation, CO coordination, and CO insertion. However, subsequent steps differ from the classical oxidative addition-reductive elimination sequence characteristic of Rh^+ . Instead, for Rh^{3+} the mechanism proceeds via H_2 adsorption followed by aldehyde formation through a σ -bond metathesis-type step, such that the formal oxidation state of rhodium remains +3 throughout the catalytic cycle. Desorption of the products regenerates the initial $\text{Z-Rh}^+-\text{H}^-$ and $\text{Z-Rh}^{3+}-\text{H}^-$ active sites. Pathways leading to linear and branched aldehydes are denoted PL and PB, respectively, and the corresponding activation free energies are summarised in Table S5.

The computed free energy profile for the $\text{Z-Rh}^+-\text{H}^-$ system is presented in Figure S24. The initial intermediate corresponds to a square-planar $\text{Rh}^+\text{H}(\text{CO})_3$ complex, which is essentially detached from the zeolite framework because the adsorption of three CO molecules onto the pre-stabilized $\text{Z-Rh}^+-\text{H}^-$ species in the silanol nest is highly exothermic, with a stabilization energy of approximately -553 kJ/mol. This large value highlights the much stronger interaction of CO with the Rh^+ center compared to the silanol groups, suggesting that the catalytic behaviour should resemble that of the homogeneous system in terms of ligand effects but the geometric confinement at the zeolite channel intersections may restrict molecular rotation and thereby enhance regioselectivity. The weak interaction between the Rh^+ complex and the framework suggests limited structural stability, especially during the hydroformylation of olefins.

In the $\text{Rh}^+\text{H}(\text{CO})_3$ mechanism, the formation of propyl intermediate (I3) has low activation

barriers, approximately 2.9 and 2.6 kJ/mol for the PL and PB pathways, with exergonic reaction free energies -27.8 and -8.2 kJ/mol respectively. Subsequent CO adsorption further stabilizes the complex by -5.2 and -64.6 kJ/mol. Intermediate I4, in contrast to the homogenous mechanism (trigonal-bipyramidal), is square planar reflecting the stabilizing effect of the zeolite framework (Figure S25 and S26). As in the homogeneous case, CO insertion (S4-5) constitutes the **rate-determining step**, with an associated barrier of 58.8 and 50 kJ/mol for PL and PB respectively. The oxidative addition of H_2 is a spontaneous one-step process, being exothermic in both pathways, PL and PB, leading to the formation of a square pyramidal Rh^{3+} hydride complex. Finally, *n*-butanal formation occurs via surmounting a low barrier of 23.6 kJ/mol, regenerating the initial square-planar $Rh^+H^-(CO)_3$ species and closing the catalytic cycle.

The computed free energy profile for the hydroformylation on $Z-Rh^{3+}-H^-$ site (Figure S24) reveals a multistep sequence in which the key elementary steps differ between the two pathways, PL and PB. The adsorption of propene (S1-2) is similarly endergonic for both routes (+25 kJ/mol). Subsequent propyl formation and CO coordination steps (S2-3 and S3-4) are spontaneous and significantly exothermic, -151.3 and -179.6 kJ/mol for PL and PB respectively, driving the system downhill toward I4. From this point, the two pathways differ: for PL, the next transformation (S4-5) occurs with a barrier of 77.9 kJ/mol and a reaction energy of 37.8 kJ/mol while for PB the corresponding step is kinetically and thermodynamically more disfavoured ($\Delta G_{act} = 148.8$, $\Delta G_{reac} = 72.8$ kJ/mol). This step is the rate-determining step for PB and thus constitutes a key selectivity-determining point, where the linear route (PL) becomes strongly preferred. Subsequent adsorption of H_2 (S5-6) is exergonic for PL (-32 kJ/mol) but endergonic for PB (+30 kJ/mol). The final formation of butanal proceeds with barriers of 92 and 56 kJ/mol for PL and PB, respectively.

Isomerization reactions are in general less favoured than hydroformylation since the transfer of C3-H atom to Rh^{3+} cation from secondary propyl intermediates compete with the exothermic adsorption of CO. In Rh^{3+} sites this adsorption is even more exothermic and thus isomerization is more strongly hindered at this active site. Furthermore, an additional key distinction between the Rh^{3+} centers stabilized within the zeolite framework and either the homogeneous Rh^{3+}

species or the Rh^+ -MFI model (which resembles the homogeneous complex in its ligand environment) is the rigidity of the coordination sphere. In the Rh^{3+} -MFI system, the ligands (siloxys and silanol groups) are spatially constrained. As a result, the H-C3 bond cleavage required for double-bond migration from $\text{C1} = \text{C2}$ to $\text{C2} = \text{C3}$ would necessitate a major ligand rearrangement, feasible for Rh^+ but not for Rh^{3+} . This geometric rigidity is thus reflected in the relatively high activation barrier calculated for alkene isomerization, 91.2 kJ/mol, implying that conversion to internal (2-) alkenes is expected to be significantly slow.

Table S5. Calculated free energy (G) and enthalpy (H) changes for reaction (ΔX_{react}) and activation (ΔX_{act}) steps at 350 K, covering all elementary steps of propene hydroformylation within the periodic MFI model. All energies are given in kJ/mol.

Step	Rh^+				Rh^{3+}			
	ΔG_{act}		ΔG_{react}		ΔG_{act}		ΔG_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	25	19.5	-	-	33.5	27.5
S2-3	2.9	2.6	-27.8	-8.2	-	-	-	-
S3-4	-	-	-95.2	-64.6	-	-	-151.3	-179.6
S4-5	58.8	50.1	33.3	28.9	77.9	148.8	37.8	72.8
S5-6	-	-	16.5	8.3	-	-	-31.6	32.3
S6-7	23.6	15.6	-51.4	-51.7	92.3	56.6	9.8	-5.6
	ΔH_{act}		ΔH_{react}		ΔH_{act}		ΔH_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	25.4	20.3	-	-	34.3	30.7
S2-3	3.7	1.1	-29.3	-11.1	-	-	-	-
S3-4	-	-	-111.5	-80.9	-	-	-169.0	-199.0
S4-5	55.2	46	26.3	25	75.2	145.7	36.8	71.0
S5-6	-	-	-11.6	-26.7	-	-	-67.2	-2.1
S6-7	19.9	19.1	-62.5	-46.7	91.6	59.8	12.3	-4.3

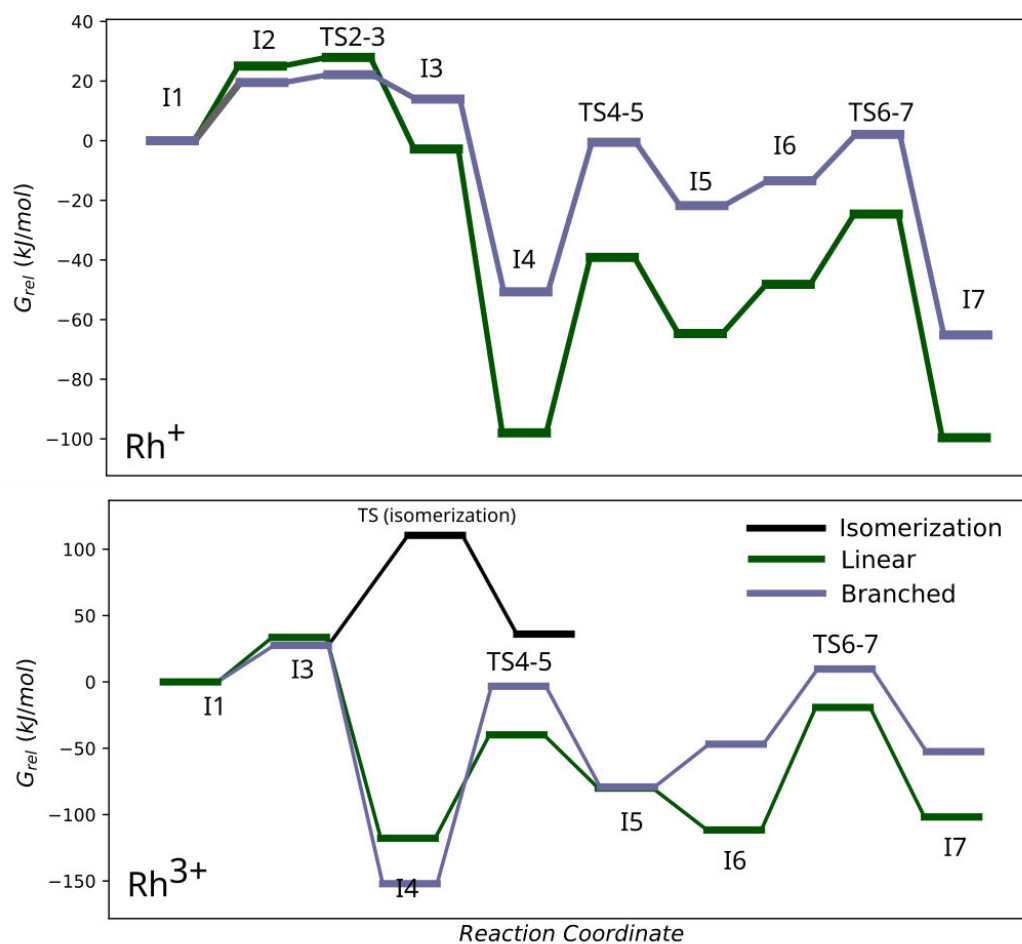


Figure S24. Energy profiles of hydroformylation on Rh^+ (upper panel) leading to the formation of n-butanal (green) and methylpropanal (violet), and on Rh^{3+} (lower panel) for n-butanal (green) and methylpropanal (violet) and isomerized alkene (black).

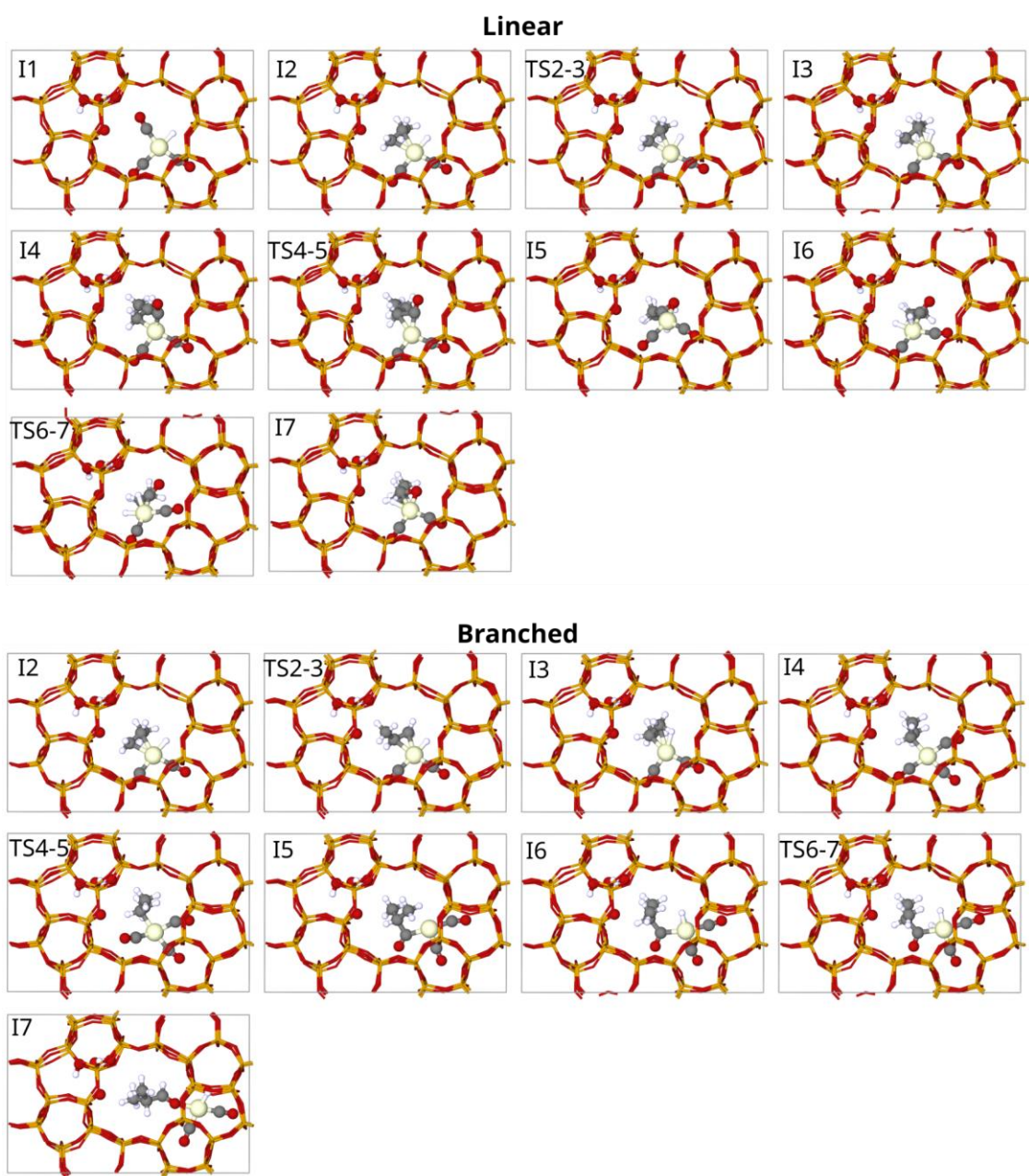


Figure S25. Optimized structures of minima involved in hydroformylation with a MFI cluster model on Rh^+ .

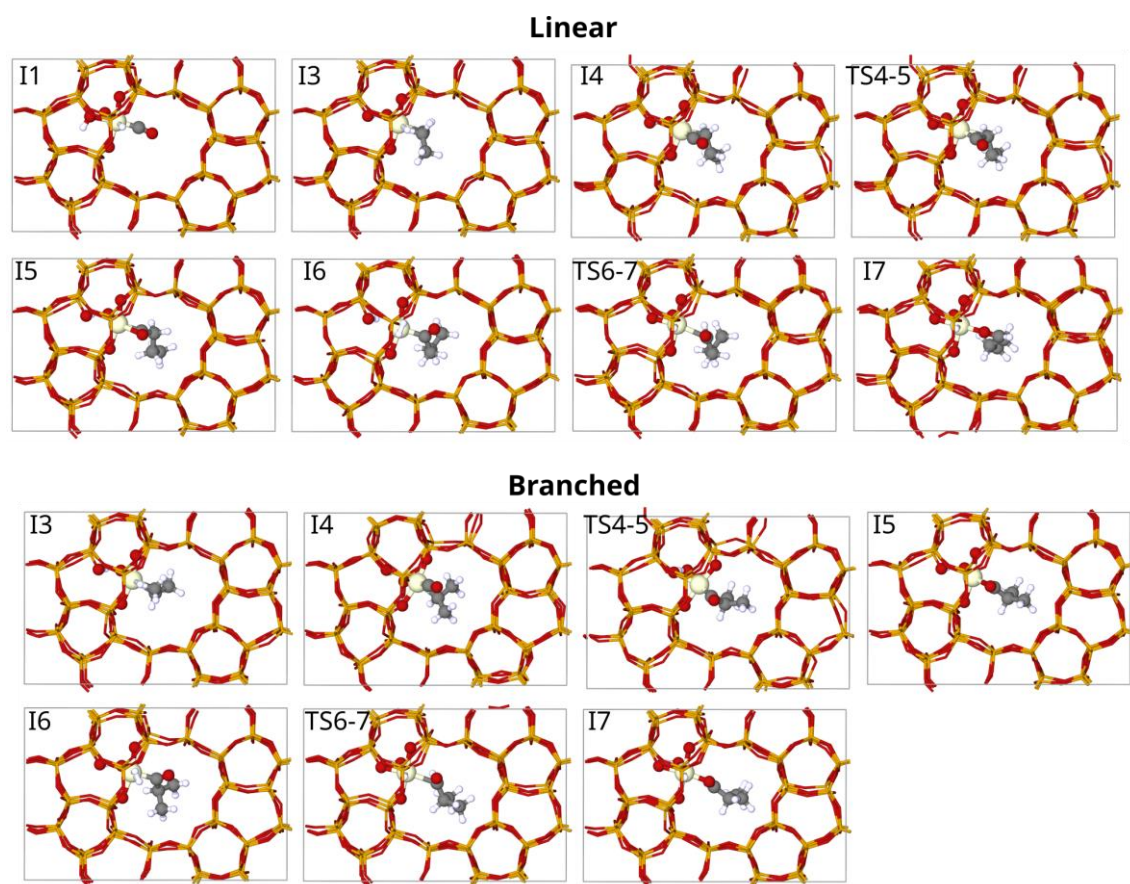
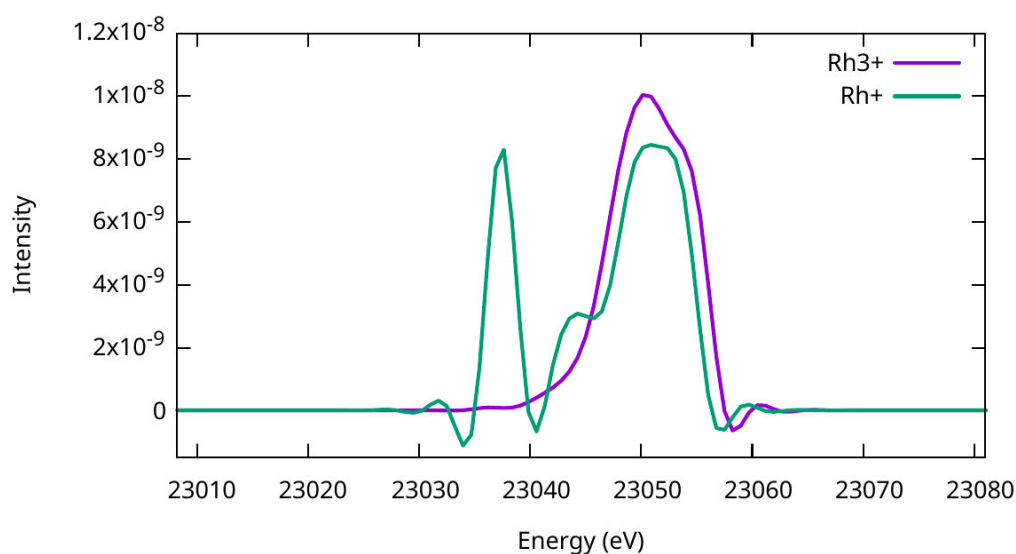


Figure S26. Optimized structures of minima involved in hydroformylation with a MFI cluster model on Rh^{3+} .

Table S6. Calculated reaction (ΔG_{react}) and activation (ΔG_{act}) free energies for all elementary steps of the hydroformylation of propene in $\text{RhH}(\text{CO})_2(\text{PH}_3)_2$. All energies are given in kJ/mol.

Step	Rh^+				Rh^{3+}			
	ΔG_{act}		ΔG_{react}		ΔG_{act}		ΔG_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	8.8				8.4	8.2
S2-3	14.1	15.6	-0.9	1.3	2.5	3.7	-1.1	-0.6
S3-4	-	-	-23.5	-25.3	-	-	-37.3	-34.2
S4-5	13.5	18.1	-1.6	-1.2	18.9	20.2	16.8	12.7
S5-6a	-	-	-3.7	-2.3	-	-	-15.7	-9.8
S6a-6b	0.0	0.0	-8.0	-9.6	-	-	-	-
S6-7	13.2	14.7	3.0	1.1	10.0	4.9	-9.8	-15.1

Regarding the XANES simulations, we performed the simulations of two models using the VASP code. The simulated spectra (below) show clear qualitative differences between the two oxidation states. The Rh^{3+} spectrum displays a sharper and more intense rising edge with a relatively narrow peak centered around ~ 23050 eV, whereas the Rh^+ spectrum shows a broader and slightly less intense feature extending over $\sim 23046\text{--}23052$ eV.



These differences can be rationalized in terms of the local electronic structure: the more electron-deficient Rh^{3+} center leads to stronger core-hole effects and more localized unoccupied states, resulting in a sharper edge feature. In contrast, Rh^+ exhibits a broader distribution of unoccupied states near the Fermi level, reflected in the more diffuse spectral shape. The relative intensity distribution and edge shape therefore qualitatively support the assignment of distinct oxidation states in our models.

Importantly, the relative energy shift between the two spectra and their distinct line shapes are in line with general experimental trends in XANES, where higher oxidation states produce edge shifts to higher energies and often more pronounced white-line features. This provides additional consistency between our atomistic models and the experimental interpretation.

However, we emphasize that these simulations should be interpreted at a qualitative level. The present approach, based on ground-state DFT electronic structure without explicit treatment of full multiple-scattering processes, does not aim to quantitatively reproduce absolute edge positions or detailed fine structure. As such, the predicted spectra are best used to identify trends and relative differences between oxidation states rather than making definitive spectral assignments.

A more rigorous and quantitative description of XANES would require dedicated methodologies (e.g., multiple scattering methods such as FEFF). Such an analysis would be a valuable direction for future studies aimed at a more direct and quantitative comparison with experiments.

We believe that these revisions significantly strengthen the manuscript and address the Reviewer's concerns.

We have included the corrections in both manuscript and Supporting Information of Section 2.11.

3) The role of N-methylpyrrolidine is discussed as a Lewis base, poisoning Rh(I) better than Rh(III) sites through coordination, hence avoiding isomerization. An alternative mechanism could be that these organic compounds could deprotonate Rh-H, hence avoiding isomerization; such pathway could be probed via computations.

Response: We thank the reviewer for this insightful suggestion and for proposing an alternative mechanistic pathway. We agree that N-methylpyrrolidine (MP) can, in principle, act as a Brønsted base and become protonated to form a stable ammonium-like species, and that such a pathway could interfere with Rh-H chemistry.

To evaluate this possibility, we have explicitly considered the deprotonation of the Rh-H species ($Z\text{-Rh}^+\text{-H}^-$) by MP. It is important to note that, within our model, the Rh-H bond is best described as a hydride species bound to a cationic Rh center. As a result, proton transfer to MP would formally generate a positive ammonium species and a negatively charged rhodium complex. Such a charge separation is expected to be

energetically unfavorable.

To quantitatively assess this mechanism, we optimized the corresponding proton-transfer structure (i.e., protonated MP) and compared it to the configuration in which MP coordinates directly to the $\text{Rh}^+\text{-H}^-$ center. The calculated energetics indicate that the proton-transfer complex is significantly less stable, by approximately 76 kJ/mol, than the MP-coordinated $\text{Rh}^+\text{-H}^-$ species. These results suggest that deprotonation of the Rh-H moiety by MP is thermodynamically disfavored and therefore unlikely to be a relevant pathway under the studied conditions. Instead, the dominant interaction is the coordination of MP to the Rh(I) center.

4) Some other minor points: energy barriers should be measured with more than 3 data points over the temperature range; graphics could be improved (e.g. how CO is bound to metal sites, local geometries...). The manuscript could likely be written in a more compact way which would enable to add the “right” details discussed above.

Response: We thank the reviewer for the valuable comment.

We have revised the Figures as referee suggested and re-write the manuscript in a more compact way. The modifications are highlighted in red in the revised manuscript.

Figure 3b-e have been updated to clearly demonstrate the coordination of CO to metal, local geometries.

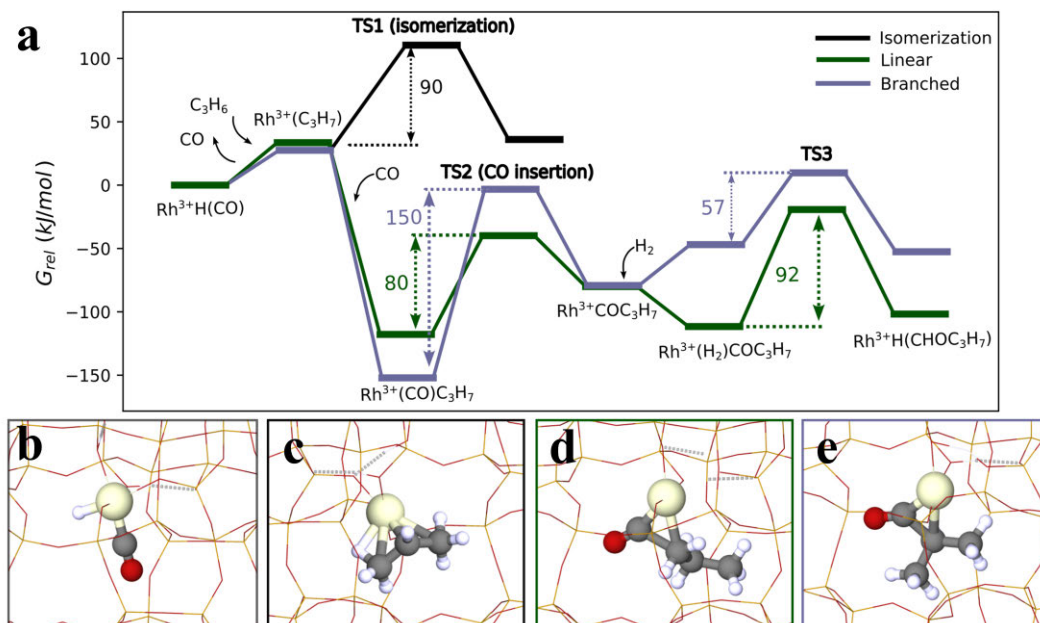


Figure 3. DFT calculation. (a) Calculated free energy profile for hydroformylation and isomerization on a Rh^{3+} single-site center embedded in the MFI zeolite model, highlighting the key elementary steps along the catalytic cycle. Free energies were calculated at 77 °C. Optimized geometries of relevant states are shown. (b) initial octahedral $Rh^{3+}-H(CO)$ intermediate. (c) TS1 showing H transfer from C3 to Rh, leading to isomerized alkene. TS2 leading to propionyl intermediate along the (d) linear and (e) branched pathways, illustrating the structural features associated with the rate-determining step of the reaction pathway. O, Rh, C, Si and H atoms are shown in red, light yellow, grey, orange and white. MFI framework is represented with lines.

Figure 4c and 4d have been updated with four data points to enable a more accurate determination of the apparent activation energy.

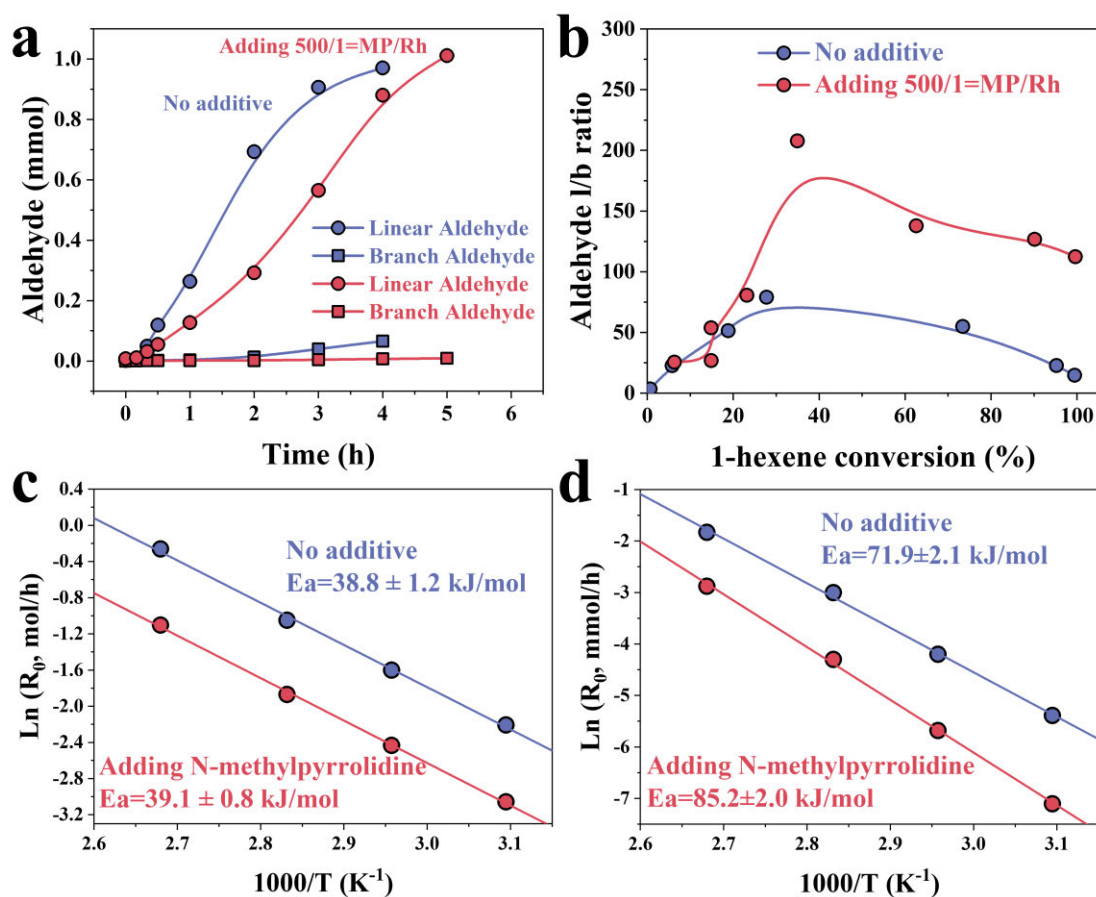


Figure 4. Time evolution profiles and apparent activation energy. (a) Time profile of linear and branched aldehydes, and (b) linear-to-branched (l/b) ratio as a function of 1-hexene conversion, during 1-hexene hydroformylation over the KRh@MFI-Cal catalyst, with and without MP. Apparent activation energy of 1-hexene (c) hydroformylation and (d) isomerization on KRh@MFI-Cal sample with and without MP (molar ratio MP/Rh = 500/1).

Reference

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2. Zhao, M. *et al.* Low-temperature hydroformylation of ethylene by phosphorous stabilized Rh sites in a one-pot synthesized Rh-(O)-P-MFI zeolite. *Nat. Commun.* **14**, 7174 (2023).
3. Zhou, Y., Doronkin, D. E., Chen, M., Wei, S. & Grunwaldt, J.-D. Interplay of Pt and Crystal Facets of TiO₂: CO Oxidation Activity and Operando XAS/DRIFTS Studies. *ACS Catal.* **6**, 7799-7809 (2016).
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7. Zhou, D.-D. *et al.* Inversed Benzene/Cyclohexene/Cyclohexane Adsorption Selectivities for One-Step Purification of Cyclohexene and Beyond. *J. Am. Chem. Soc.* **147**, 17342-17349 (2025).
8. Clark, A. H., Imbao, J., Frahm, R. & Nachtegaal, M. ProQEXAFS: a highly optimized parallelized rapid processing software for QEXAFS data. *J. Synchrotron Radiat.* **27**, 551-557 (2020).

The authors appreciate the referee's effort and time for the critical review of the manuscript again. The manuscript has been updated with new information and a point-to-point answer to all the comments risen by the referees is included in this document in red color.

All changes done in the manuscript are marked in red in the revised version.

Referee #1

Comments:

Zhao et al. have submitted a revised manuscript focusing on olefin hydroformylation catalyzed by K-Rh@MFI composites. I appreciate the authors' detailed point-by-point response to previous reviewer comments as well as the substantial supplementary experimental data added in this revised version, which fully reflects the authors' dedicated efforts to address all prior concerns raised in the first round of review. Nevertheless, several critical scientific issues still remain unresolved. Despite the noticeable improvement of this manuscript, further targeted revisions are still indispensable to consolidate the research conclusions and meet the rigorous publication standards of Nature.

Response: We sincerely thank the reviewer for the positive and encouraging evaluation of our work, and appreciate the recognition of our efforts to improve the quality of the manuscript.

1) Supplementary catalytic performance comparison. The authors have not provided comparative hydroformylation results of Rh@FER catalysts with and without NMP additives. Given that the authors attribute catalytic differences to zeolite channel size effects, supplementary catalytic tests of Rh@FER with and without MP additives are highly required for systematic validation.

Response: We thank the reviewer for the valuable comment. Following the reviewer's suggestion, we carried new experiments with and without MP and NMP on Rh@FER

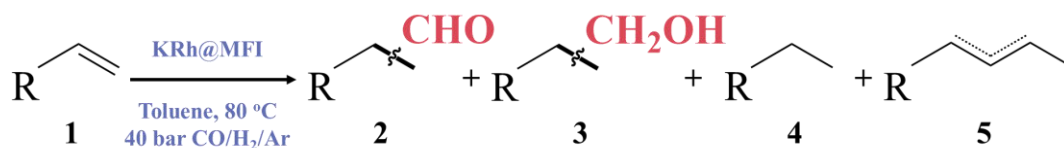
and Rh@FAU catalysts.

As shown in the newly added results, both Rh@FER and Rh@FAU exhibit pronounced olefin isomerization. Upon the addition of MP or NMP, both the isomerization and hydroformylation activities are significantly reduced (see Table R1), while the suppression of the olefin isomerization is not so relevant as before. This could be related on the one hand to an accumulation of MP/NMP inside the zeolite channels (as found from the elemental analysis, see response to question 5, Table R3), which restrict the access of the olefin to the active sites lowering catalytic activity, and on the other hand to a different local environment of Rh^+ (as evidenced from the IR-CO studies, see response to question 2), which makes MP/NMP interaction weaker and not so efficient as in the KRh@MFI zeolite.

Thus, the additives alone are not enough to achieve high regioselectivity. Instead, the combination of the MFI zeolite topology (silicalite-1), confined Rh^{3+} active sites, and MP/NMP additives are essential for highly regioselective α -olefin hydroformylation.

The corresponding results and discussion on the effects of different zeolite topologies have been added to the Supporting Information of **“Appendix 3.5. 1-Decene hydroformylation on Rh@zeolite with different topology type zeolite”**.

Table R1. Catalytic results for KRh@MFI-Cal, Rh@Na-FER-Cal, and Rh@Na-FAU catalysts of 1-decene hydroformylation at 80 °C.^a



Entry	Catalysts	Conv. (%)	Selec. (%) Aldehyde (L) ^b	l/b ^c	Yield (%)				R ₀ (mmol/h) ^d L-Aldehyde	R ₀ (mmol/h) ^d Iso-Alkenes	TON ^e	TOF (h ⁻¹) ^f
					2	3	4	5				
1	KRh@MFI-Cal	99.4	92.1 (89.2)	30	91.6	0	1.2	6.6	0.85	0.036	2137	2096
2	KRh@MFI-Cal-500MP	98.5	96.8 (96.5)	378	95.3	0	0.5	2.6	0.82	0.018	2279	2052
4 ^g	KRh@MFI-Cal-4000NMP	99.8	95.9 (95.8)	817	95.7	0	1.0	3.1	0.67	0.017	2406	1706
5 ^h	Rh@Na-FER-Cal	74.5	57.2 (39.3)	2.2	42.6	0	0.2	31.7	0.02	0.040	1543	87
6 ^h	Rh@Na-FER-Cal-500MP	7.8	70.7 (66.3)	15	5.5	0	0.3	2.0	1.4×10 ⁻³	0.19×10 ⁻³	199	7
7 ^h	Rh@Na-FER-Cal-4000NMP	1.3	45.4 (34.8)	3.3	0.6	0	0	0.7	0.5×10 ⁻³	0.27×10 ⁻³	211	2
8 ⁱ	Rh@Na-FAU-Cal	99.3	63.6 (38.2)	1.5	63.1	0	1.5	34.7	0.08	0.117	1523	310
9 ^j	Rh@Na-FAU-Cal-500MP	73.2	53.3 (39.9)	3.0	39.0	0	0.5	33.8	0.07	0.08	790	172
10 ^h	Rh@Na-FAU-Cal-4000NMP	15.4	50.6 (40.9)	4.3	7.8	0	0.2	7.4	0.01	0.008	321	22

^a Reaction conditions: 1 mmol LAO, 20 mg catalyst, 20 mg isooctane (internal standard), 4 mL toluene, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm and 3h reaction.

^b Total aldehyde selectivity (L=Linear aldehyde selectivity).

^c Ratio of the linear aldehyde to the branched aldehyde.

^d Reaction rate for linear aldehyde formation and reaction rate for isomerized alkenes formation, mmol/h, calculated when LAO conversion is < 20%.

^e mmol of linear aldehyde/total mmol of Rh at 3h reaction time.

^f Rate for the formation of linear aldehyde/total mmol of Rh.

^g 9h reaction.

^h 22h reaction.

ⁱ 7h reaction.

^j 6h reaction.

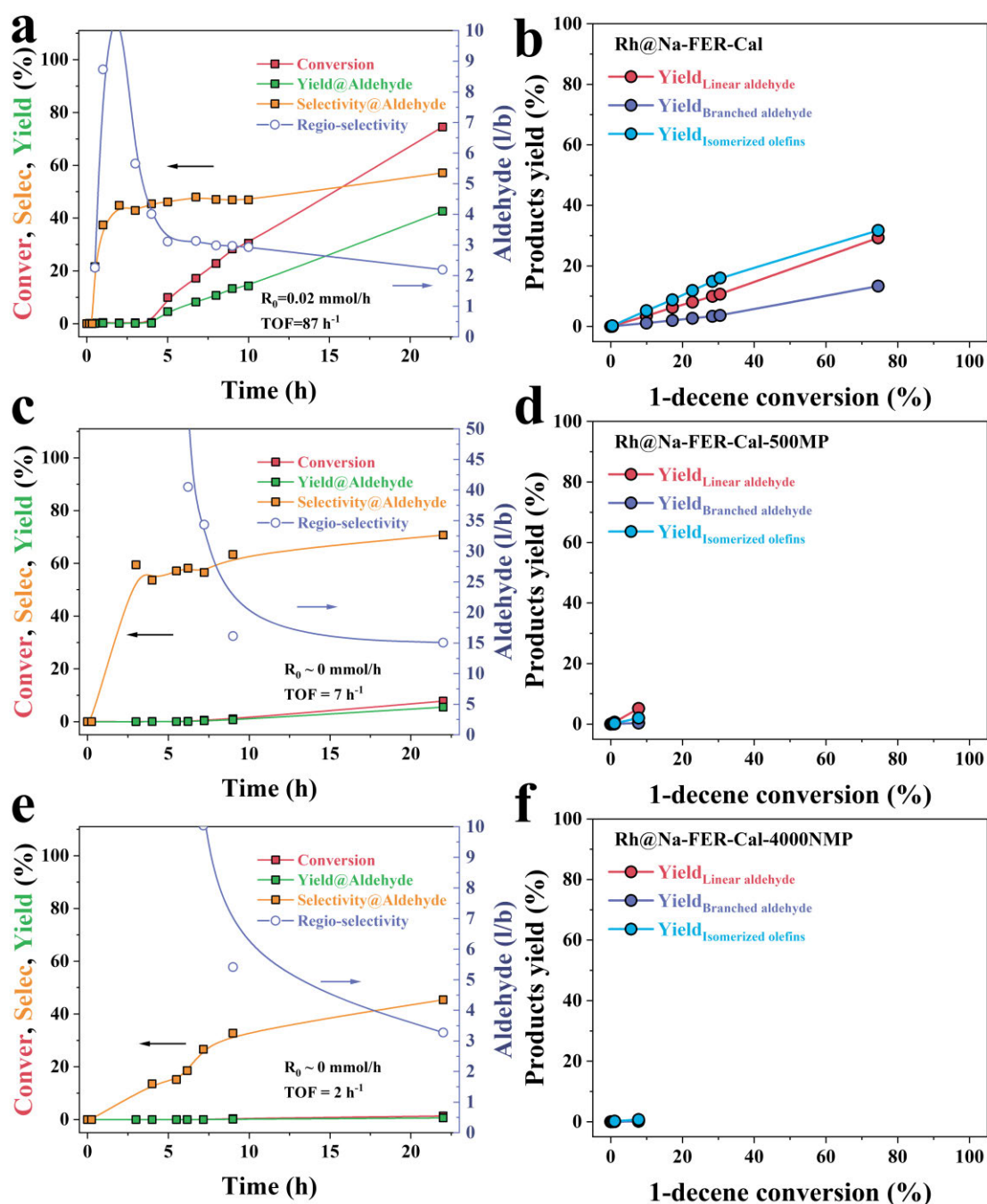


Figure R1. 1-Decene hydroformylation: (a) Time profiles of activity on Rh@Na-FER-Cal catalyst and (b) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (c) Time profiles of activity Rh@Na-FER-Cal-500MP catalyst and (d) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (e) Time profiles of activity Rh@Na-FER-Cal-4000NMP catalyst and (f) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. Reaction condition: 1 mmol LAO, 20 mg catalyst, 20 mg isooctane (internal standard), 4 mL toluene, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm, R_0 , TOF and TON are values for linear aldehyde formation.

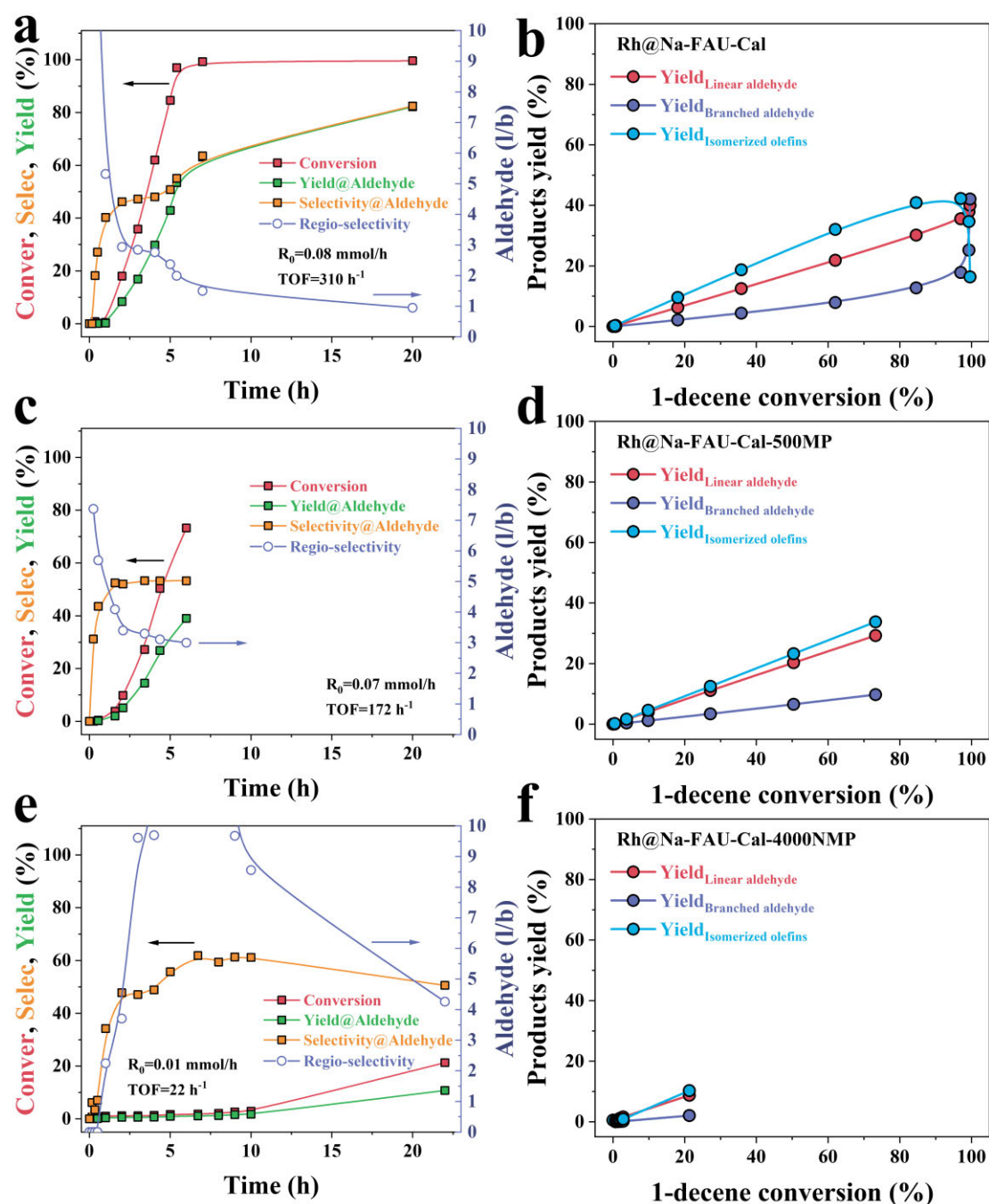


Figure R2. 1-Decene hydroformylation: (a) Time profiles of activity on Rh@Na-FAU-Cal catalyst and (b) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (c) Time profiles of activity Rh@Na-FAU-Cal-500MP catalyst and (d) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. (e) Time profiles of activity Rh@Na-FAU-Cal-4000NMP catalyst and (f) yield of linear aldehyde, branched aldehyde, isomerized olefins as a function of 1-decene conversion. Reaction condition: 1 mmol LAO, 20 mg catalyst, 20 mg isooctane (internal standard), 4 mL toluene, 40 bar CO/H₂/Ar (45/45/10 vol%), 80 °C, 800 rpm, R_0 , TOF and TON are values for linear aldehyde formation.

2) Lack of CO-IR characterization evidence. The authors have synthesized and compared Rh-based catalysts supported on zeolites with diverse topological structures. However, CO infrared spectroscopy (CO-IR), the most direct and convincing characterization technique to verify the blocking effect toward Rh^+ active sites, is absent in this work. Supplemental CO-IR spectra will provide solid spectroscopic evidence to support the authors' core hypothesis of Rh^+ site blocking.

Response: We thank the referee meaningful comment. As suggested by the referee, we did IR-CO studies on the Rh@Na-FER-Cal and Rh@Na-FAU-Cal samples, after reaction in the presence of MP and compared to the corresponding samples in absence of MP additive.

In the case of the Rh@Na-FER-Cal sample (Figure R3), both Rh^{3+} (2137 cm^{-1}) and Rh^+ (2114 and 2047 cm^{-1}) are not influenced by the addition of MP. Furthermore, the $\text{Rh}^+(\text{CO})_2$ dicarbonyl vibration appears at 2114 and 2047 cm^{-1} , which differs to that obtained in the KRh@MFI-Cal-500MP sample (2065 and 1996 cm^{-1}). These differences are related to the different Rh^+ Lewis acidity related to the different zeolite topology.

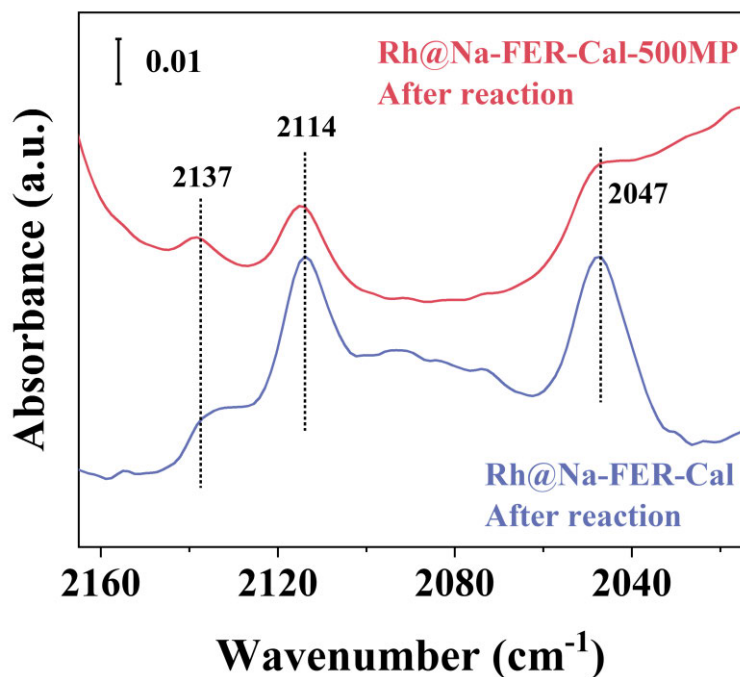


Figure R3. IR-CO at -65°C and 2 mbar CO coverage spectra for Rh@FER-Cal and Rh@FER-Cal-500MP after 1-decene hydroformylation reactions.

In the case of the Rh@Na-FAU-Cal sample, the only signal we found is relative to $\text{Na}^+\text{-CO}^{\text{I}}$ (2171 cm^{-1} ; see Figure R4), which is due to the high Na loading in the sample (10.6wt% Na loading based on ICP-OES analysis, Supplementary Table 22).

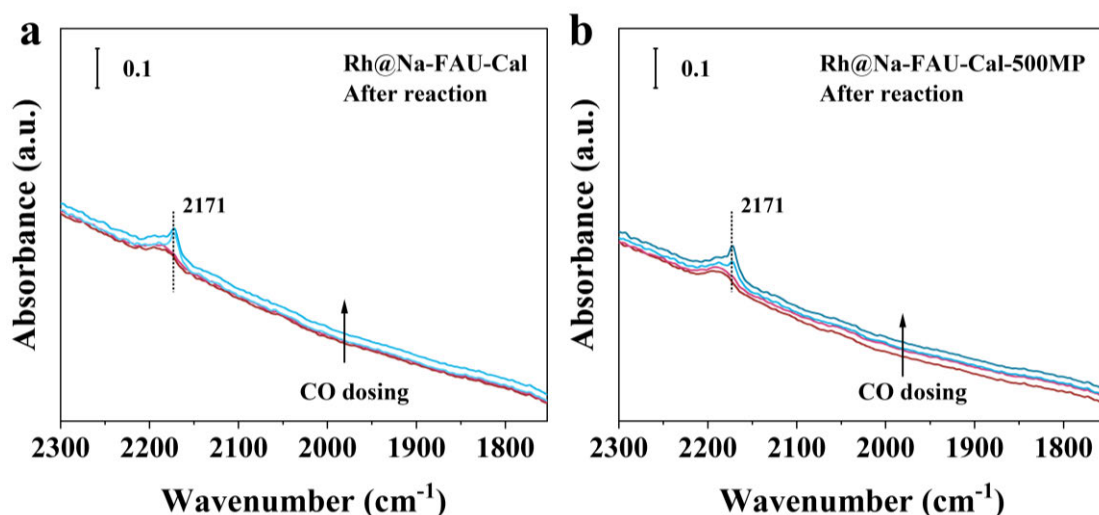


Figure R4. IR-CO at -65°C and at increasing CO coverage (0.01-2 mbar) for (a) Rh@Na-FAU-Cal and (b) Rh@Na-FAU-Cal-500MP after 1-decene hydroformylation reactions.

The corresponding IR result and discussion have been added to the Supporting Information of “**Appendix 3.5. 1-Decene hydroformylation on Rh@zeolite with different topology type zeolite**”.

3) Verification of Rh dispersion via CO chemisorption. To reliably validate the claimed 100% dispersion of rhodium species on the support, CO chemisorption tests are suggested. At minimum, such measurements should be conducted on the pristine additive-free Rh@MFI catalyst to quantify the actual metal dispersion.

Response: We thank the reviewer for the comment. CO chemisorption measurements were performed using the double-isotherm method on an Anton Paar Autosorb 6200 FKM MP analyzer. Prior to adsorption, the samples (200-300 mg) were degassed in situ under vacuum (1.33 Pa) at 80 °C for 2h and then cooled to 25 °C. KRh@MFI-CalRed was in situ reduced in a 10 mL/min flow of pure H₂ at 600 °C for 2h. Pure CO was subsequently introduced to record the first adsorption isotherm, corresponding to the total CO uptake. After evacuation under vacuum at 25 °C to remove reversibly adsorbed CO, a second adsorption isotherm was recorded to determine the reversible CO uptake. The amount of irreversibly chemisorbed CO was obtained from the difference between the two isotherms. The adsorption isotherms were collected over a pressure range of (0.5-11)×10⁴ Pa.

Table R2. CO chemisorption results on KRh@MFI catalysts.

Sample	Rh loading (wt%)	Theoretical Rh atoms (μmol/g)	Experimental irreversibly chemisorbed CO (μmol/g)	Experimental/Theoretical Rh ratio (%)
KRh@MFI-Cal	0.2	19.4	4.0	21 ^a
KRh@MFI-CalRed	0.2	19.4	32.6	84 ^b
KRh@MFI-Cal (After reaction)	0.2	19.4	1.0	5 ^a

^a CO/Rh stoichiometric ratio of 1.

^b CO/Rh stoichiometric ratio of 2.

For the KRh@MFI-Cal catalyst containing Rh₂O₃ clusters, the amount of irreversibly chemisorbed CO is substantially lower than the theoretical value (see Table R2), which is due to the low interaction of CO with oxidized Rh species.

In contrast, the reduced KRh@MFI-CalRed catalyst containing metallic Rh⁰ domains, exhibits a much higher apparent Rh dispersion (84%), consistent with a good metal dispersion and the strong CO interaction with Rh⁰.

In the KRh@MFI-Cal sample after reaction the amount of irreversibly chemisorbed CO is extremely low. That is because under hydroformylation reaction conditions, the confined Rh₂O₃ clusters in KRh@MFI-Cal is disrupted into isolated Rh³⁺-CO and Rh⁺(CO)₂ species, as demonstrated by IR-CO results. The fact that Rh⁺ and Rh³⁺ becomes already titrated with CO after reaction, explain the low CO uptake during the CO chemisorption studies in the KRh@MFI-Cal sample after reaction (Entry 3, Table R2).

Based on this data, we may conclude that determination of the Rh dispersion based on CO chemisorption on fresh and spent KRh@MFI-Cal catalysts, are significantly underestimated and cannot be used to calculate metal dispersion.

In our study, the initially formed Rh₂O₃ clusters undergo in situ disruption into isolated Rh³⁺ and Rh⁺ species under hydroformylation reaction conditions. Consequently, it is reasonable to assume that the Rh species are predominantly atomically dispersed during the reaction, in agreement with analogous Rh systems reported in the literature²⁻⁵.

4) Simplification of catalyst nomenclature. The current complex naming rules for catalysts severely hinder manuscript readability. Representative complicated labels including KRh@MFI-CalRed-CO and KRh@MFI-Cal-Toluene-CO/H₂ bring unnecessary obstacles for readers to distinguish different catalyst samples. The authors are suggested to adopt a more concise and unified naming system to clarify sample differences and improve the overall readability of the full text.

Response: We thank the reviewer for the comment. In this work, the KRh@MFI catalyst

undergoes different pretreatment sequences, including calcination, reduction and CO exposure, as well as CO/H₂ treatment in toluene in order to selectively modify the type of Rh species.

To maintain consistency and clarity in sample nomenclature, we therefore retain the abbreviations Cal and Red to denote calcination and reduction steps, respectively. Additionally, the sample pretreated in H₂ flow at 600 °C for 3h followed by CO treatment at 90 °C for 2h is denoted as “KRh@MFI-CalRed-CO”.

As requested by the referee, to simplify the notation for the sample pre-treated under 40 bar CO/H₂ in toluene for 2h, we have renamed it as “KRh@MFI-Cal-CO/H₂”. The corresponding pretreatment details are clearly described in the manuscript.

“KRh@MFI-Cal-CO/H₂” has been updated in manuscript and Supporting Information.

5) Mechanistic discussion on excessive MP dosage. As listed in Table S8, the optimal MP/Rh molar ratio for achieving the highest linear-to-branched aldehyde (l/b) ratio ranges from 500 to 1000. If the N-methyl functional group of MP molecules indeed coordinates with Rh⁺ active sites as proposed, the requirement for such a huge excess of MP cannot be reasonably explained. It is recommended to conduct CHNS elemental analysis on spent catalysts to quantify the residual MP content, and further calculate the actual MP/Rh molar ratio after catalyst preparation and catalytic reactions, so as to clarify the coordination mechanism between MP and Rh active centers.

Response: We thank the reviewer for this insightful comment. Following the reviewer's suggestion, CHNS elemental analysis was performed on the spent catalysts to quantify the residual MP content after hydroformylation reaction. After reaction, the samples were cooled down, depressurized, and washed several times with toluene. During these post-treatment processes, the weakly coordinated MP molecules and the free MP molecules physically confined inside the MFI channels were mostly desorbed and washed away. The residual MP/Rh molar ratio on the spent catalyst determined by CHNS elemental analysis is 15-19 (Table R3, assuming that all detected nitrogen

originates exclusively from the MP additive), which is significantly lower than the initial feeding ratio (500-1000). Furthermore, the Rh free K-MFI-Cal-500MP (after reaction) gives similar nitrogen amount, which indicates that the MP coordinated to Rh should be at least stoichiometric molar ratio.

The excessive MP dosage is required because hydroformylation is performed under elevated temperatures and high CO/H₂ pressures, where CO behaves as a strongly ligand and continuously competes with MP (or NMP) for Rh⁺ coordination sites. As a result, ligand exchange between CO and MP is inevitable under reaction conditions. According to Le Chatelier's principle, maintaining a large excess of MP in the liquid phase (MP/Rh > 500) is thermodynamically necessary to shift the equilibrium toward the MP-coordinated Rh⁺ state. This high ligand concentration continuously replenishes the Rh⁺-MP complexes as MP is displaced by CO during catalysis, thereby ensuring persistent suppression of the isomerization-active Rh⁺ species throughout the reaction.

In addition to the stoichiometric Rh-MP complex, MP can also interact with MFI through silanol groups ($\equiv$ Si-OH). The residual MP molecules, particularly those located in the vicinity of Rh⁺ centers, may also create a sterically confined microenvironment that suppresses α -olefin insertion into Rh⁺-H(CO)₂-MP intermediates and inhibits the undesired olefin isomerization pathway catalyzed by Rh⁺.

Taken together, these results demonstrate the necessity of using a higher than the stoichiometric dosage of MP/NMP in the reaction. Once the isomerization activity associated with Rh⁺ species is effectively suppressed through MP/NMP coordination, the remaining accessible Rh³⁺ species predominantly catalyze the hydroformylation of α -olefins to linear aldehydes. More importantly, the outstanding regioselectivity cannot be attributed to a single factor, but rather arises from the synergistic interplay among the specific pore dimensions of the MFI zeolite, the coordination of the -N-methyl organic additives (MP/NMP), and intrinsically highly regioselective Rh³⁺ species. Together, these factors are responsible for the exceptionally high linear-to-branched aldehyde ratio achieved in this catalytic system.

We have added the above comments in the Supporting Information, Section 2.21 (Page 67) for explanation of excessive MP dosage in addition with the CHNS data in Supplementary Table 9.

Table R3. Elemental analysis results on KRh@MFI and Rh@Na-FER catalysts.

Sample	C (wt%) ^a	H (wt%) ^a	N (wt%) ^a	S (wt%) ^a	Rh (wt%) ^b	MP/Rh molar ratio ^c
K-MFI-Cal-500MP	2.46	0.48	0.29	0	0	-
KRh@MFI-Cal (Before reaction)	1.44	0.29	0	0	0.2	0
KRh@MFI-Cal-500MP (After reaction)	8.47	1.49	0.52	0	0.2	19
KRh@MFI-Cal-MP solvent (After reaction)	2.83	0.58	0.41	0	0.2	15
KRh@MFI-Cal-4000NMP (After reaction)	8.62	1.50	0.29	0	0.2	11
Rh@Na-FER-500MP (After reaction)	2.10	1.37	0.78	0	0.1	57
Rh@Na-FER-4000NMP (After reaction)	1.90	1.34	0.62	0	0.1	46

^a Measured by elemental analysis.

^b Measured by ICP-OES.

^c The MP content was calculated based on the nitrogen content, and the molar ratio of residual MP to Rh in the catalyst was determined.

6) EXAFS spectra fitting and structural parameter analysis. The Rh K-edge EXAFS spectra displayed in Figure 2h and Figure S59b cover three key samples: post-reaction KRh@MFI-Cal, post-reaction KRh@MFI-Cal-500MP, and CO-treated KRh@MFI-CalRed-CO. All these EXAFS curves need to be quantitatively fitted to extract key structural parameters, including coordination number, interatomic distance and Debye-Waller factor. The fitting results will help elucidate the detailed local coordination environment of Rh active centers, especially the Rh-O and Rh-C coordination shells around rhodium sites if possible.

Response: We thank the reviewer for the careful evaluation, and we agree that the EXAFS quality and the available energy range allow for a deeper structural parameter analysis. Best fit models were determined using a grid search with fixed values for path coordination numbers by employing Larch, the Python implementation of Artemis, and are now included in the Supporting Information, while the fitting procedure has been described in the Methods section.

The results complement and support the XANES region analysis (Appendix 3.4). Details on the local structure can be now addressed. The obtained coordination numbers reflect the amount of the different bonds in the different systems, where higher numbers correspond to higher percentages.

Methods:

“Extended X-ray absorption fine structure (EXAFS) were extracted using the AUTOBK algorithm employing a spline in the range of 0 to 15.9 Å⁻¹ having an R_{bkg} of 1.05. The FEFF6 code^{6,7} was used for scattering path generation, and multi (k¹, k², k³)-weighted fits of the data were carried out in r-space over r- and k- ranges as indicated in the Supporting Information. The S₀² value was set to 0.9, and a global E₀ was employed with the initial E₀ value set to the maximum inflection point of the rising edge. Single scattering paths were fit in terms of a Δ_{reff} and σ², which represent the deviation from the expected interatomic distances and the structural disorder, respectively. Co-linear Rh-C=O paths were fit with a common Δ_{reff} and σ². To assess the goodness of the fits both the R_{factor} (%R) and the reduced χ² (χ²_v) were minimized, with a number of variables always below the limit imposed by the Nyquist theorem ($\frac{2\Delta k \Delta r}{\pi}$), ensuring that the data was not over-fit. Best fit models were determined using a grid search with fixed values for path coordination numbers (CN) by employing Larch, the Python implementation of Artemis⁸.”

The corresponding EXAFS fitting results have been added to the Supporting Information of “[Appendix 3.4](#)”.

Table R4. EXAFS analysis using Multi (k^1 , k^2 , k^3)-weighted fits carried out in r-space (1-3.2 Å) over a k-range of 3-13.5 Å⁻¹ using a Hannings window (dk 1), and $S_0^2 = 0.9$. Bond distances and disorder parameters (Δr_{eff} and σ^2) were allowed to float having initial values of 0.0 Å and 0.003 Å² respectively, with a universal E_0 and $\Delta E_0 = 0$ eV.

KRh@MFI-Cal (Before reaction)						
	R _{FACTOR}	X ² _v	Var. No.	k-range (Å ⁻¹)	r-range (Å)	ΔE ₀ (eV)
	0.023	15.7	4	3-13.5	1-3.2	−3.4(1.3)
PATHS						
Rh-C/N/O	CN	r (Å)		σ ² (x10 ³ Å ²)		
	4.8	2.04 (0.01)		3.0 (0.5)		
Rh-Rh	CN	r (Å)		σ ² (x10 ³ Å ²)		
	1.0	3.09 (0.01)		4.6 (1.3)		
KRh@MFI-CalRed-CO						
	R _{FACTOR}	X ² _v	Var. No.	k-range (Å ⁻¹)	r-range (Å)	ΔE ₀ (eV)
	0.009	0.8	7	3-13.5	1-3.2	−5.6 (0.7)
PATHS						
Rh-C (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	0.85	1.79 (0.01)		3.4 (1.3)		
Rh-O (Rh ₂ O ₃)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	1.0	1.93 (0.01)		5.0 (1.2)		
Rh-Rh (Rh ⁰)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	2.0	2.73 (0.01)		5.7 (0.4)		
Rh-O (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	0.85	2.94 (0.01)		3.4 (1.3)		
Rh-O-C (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	1.28	2.94 (0.01)		3.4 (1.3)		

KRh@MFI-Cal (After reaction)

	R_{FACTOR}	X²_v	Var. No.	k-range (Å⁻¹)	r-range (Å)	ΔE₀ (eV)
	0.011	1.3	7	3-13.5	1-3.2	-4.8 (0.8)

PATHS

Rh-C	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	0.8	1.80 (0.01)	2.6 (1.3)
Rh-O	CN	r (Å)	σ² (x10³ Å²)
(Rh ₂ O ₃)	1.9	2.0 (0.01)	6.6 (1.0)
Rh-Rh	CN	r (Å)	σ² (x10³ Å²)
(Rh ⁰)	2.0	2.72 (0.01)	5.6 (0.4)
Rh-O	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	0.8	2.95 (0.01)	2.6 (1.3)
Rh-O-C	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	1.2	2.95 (0.01)	2.6 (1.3)

KRh@MFI-Cal-500MP (After reaction)

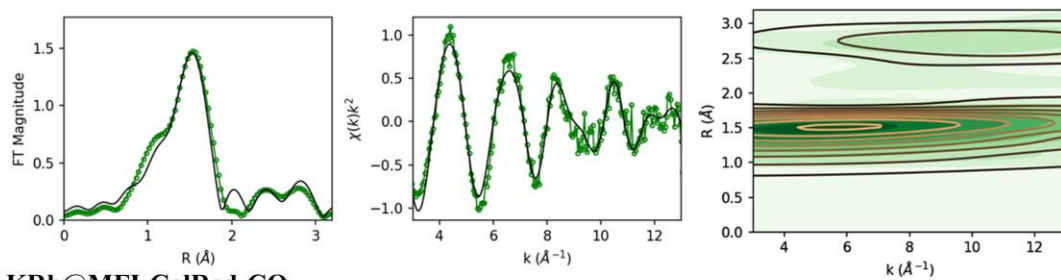
	R_{FACTOR}	X²_v	Var. No.	k-range (Å⁻¹)	r-range (Å)	ΔE₀ (eV)
	0.014	1.6	7	3-13.5	1-3.2	-3.4 (1.0)

PATHS

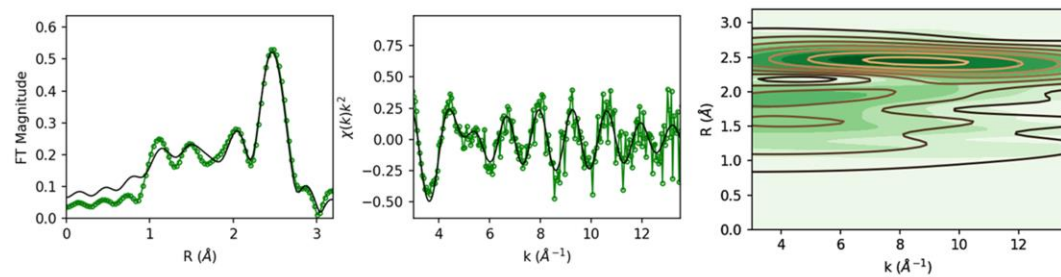
Rh-C	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	0.5	1.80 (0.02)	3.1 (2.5)
Rh-O	CN	r (Å)	σ² (x10³ Å²)
(Rh ₂ O ₃)	2.0	2.01 (0.01)	5.5 (0.8)
Rh-Rh	CN	r (Å)	σ² (x10³ Å²)
(Rh ⁰)	2.0	2.71 (0.01)	6.2 (0.6)
Rh-O	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	0.5	2.95 (0.02)	3.1 (2.5)
Rh-O-C	CN	r (Å)	σ² (x10³ Å²)
(Rh-CO)	0.75	2.95 (0.02)	3.1 (2.5)

KRh@MFI-Cal-CO/H ₂						
	R _{FACTOR}	X ² _v	Var. No.	k-range (Å ⁻¹)	r-range (Å)	ΔE ₀ (eV)
	0.018	15.7	7	3-13.5	1-3.2	-1.1 (1.6)
PATHS						
Rh-C (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	0.55	1.86 (0.03)		4.0 (3.6)		
Rh-O (Rh ₂ O ₃)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	2.1	2.03 (0.01)		5.7 (1.0)		
Rh-Rh (Rh ⁰)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	2.0	2.75 (0.01)		4.4 (1.2)		
Rh-O (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	0.55	3.0 (0.03)		4.0 (3.6)		
Rh-O-C (Rh-CO)	CN	r (Å)		σ ² (x10 ³ Å ²)		
	0.83	3.0 (0.03)		4.0 (3.6)		

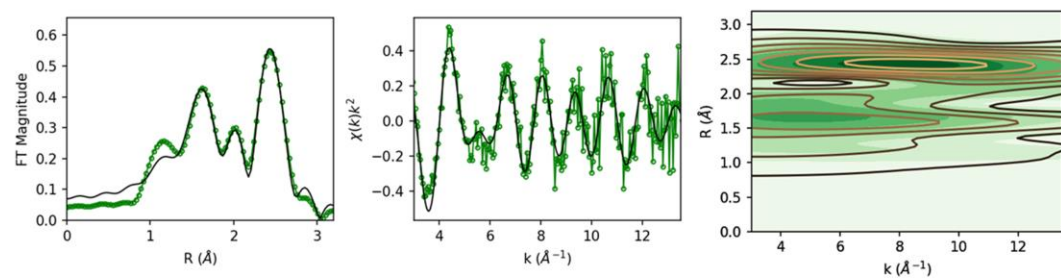
KRh@MFI-Cal (Before reaction)



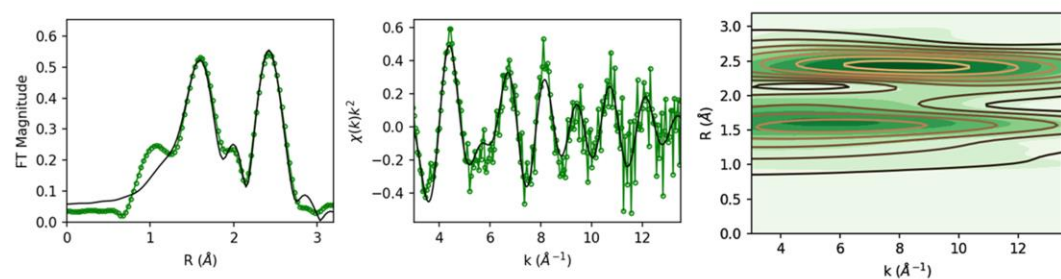
KRh@MFI-CalRed-CO



KRh@MFI-Cal (After reaction)



KRh@MFI-Cal-500MP (After reaction)



KRh@MFI-Cal-CO/H₂

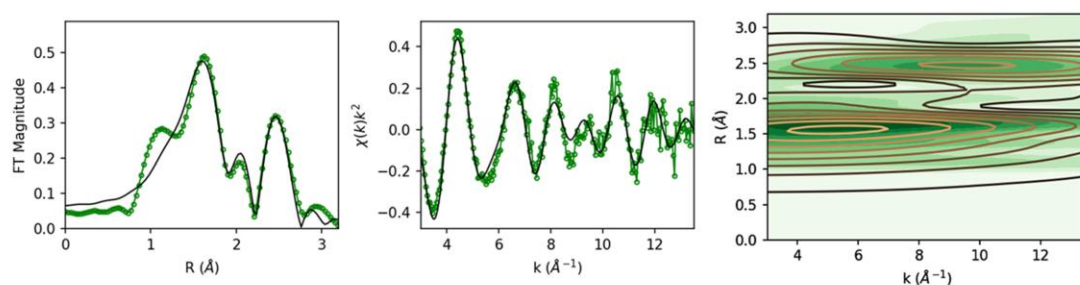


Figure R5. EXAFS fit of Krh@MFI samples presented in Table R4.

Referee #2

Comments:

The authors have put a lot of effort to answer many questions raised by the reviewers, and the manuscript has certainly significantly improved. Further improvements are still required before possible publication in Nature.

Response: We sincerely thank the reviewer for the positive evaluation of our work and appreciate the recognition of our efforts to improve the quality of the manuscript.

1) In contrast to the answer of the authors, I could not find any information about the enthalpies, only Gibbs free energy (Table S5 and S6 and associated figure). The Reviewer thinks it is essential to provide both considering that entropy is very difficult to calculate and the actual energy landscape likely lies in between these two values; it is also a good way to gauge how much entropy is driving the processes.

Response: We thank the Reviewer for this observation. We apologize for the lack of clarity in our previous response. Providing both thermodynamic quantities allows a direct assessment of the entropic contribution to the free-energy landscape and facilitates comparison between the enthalpy-driven and entropy-driven components of the reaction mechanism.

Please note that the enthalpy values for the periodic MFI models were already included in Table S5 of the Supporting Information. Table S5 reports both Gibbs free energies and enthalpies. The free-energy data are listed as ΔG_{act} and ΔG_{reac} for the Rh^+ and Rh^{3+} pathways. Further down in the Table (beginning at row 9), the corresponding enthalpy values are reported as ΔH_{act} and ΔH_{reac} for both Rh^+ and Rh^{3+} species. We apologize if this was not sufficiently clear in the previous version.

However, the Reviewer is correct that Table S6 only reported Gibbs free energies and did not include the corresponding enthalpies. Table S6 referred to the mechanism of Rh^+ and Rh^{3+} complexes and a more consistent presentation would be achieved by merging Table S6 and Table S4 to have the same format as Table S5 (both free energy

and enthalpy in same Table). Following the Reviewer's recommendation, we have now merged Table S6 in Table S4, and now Table S4 reports the free energy and enthalpy values for homogenous mechanisms so that it follows the same format as Table S5.

In summary, the revised Supporting Information contains **Supplementary Table 4** with free energy and enthalpy for the homogenous mechanisms and **Supplementary Table 5** with the free energy and enthalpy calculated with the periodic models of MFI. We have updated the caption of the Tables to specifically mention that both contain free energy and enthalpy. The Tables in the revised Supporting Information are included as follows:

Supplementary Table 4. Calculated free energy (G) and enthalpy (H) changes for reaction (ΔX_{react}) and activation (ΔX_{act}) steps at 300 K, covering all elementary steps of propene hydroformylation with the isolated complex models $\text{RhH}(\text{CO})_2(\text{PH}_3)_2$ and $\text{RhH}(\text{OH})_2(\text{PH}_3)_2$. All energies are given in kJ/mol.

Step	Rh^+				Rh^{3+}			
	ΔG_{act}		ΔG_{react}		ΔG_{act}		ΔG_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	46.8		-	-	41.5	42
S2-3	48.9	56.4	0.4	5.4	4.6	8.0	-0.4	-1.3
S3-4	-	-	-43	-53.1	-	-	-97.2	-83.8
S4-5	49.7	71.6	-4.18	-2.5	72.1	80.4	60	46
S5-6a	-	-	31	36.8	-	-	-10.1	11.3
S6a-6b	-	-	-29.7	-35.9	-	-	-	-
S6-7	44.7	53.4	1.7	-3.3	40.6	15.9	-30.6	-55.2
	ΔH_{act}		ΔH_{react}		ΔH_{act}		ΔH_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	37.3		-	-	34.9	34.2
S2-3	56.2	62.7	5.0	8.8	8.4	13.1	-1.5	-0.4
S3-4	-	-	-91.6	-99.6	-	-	-144	-131.5
S4-5	57.5	75.4	-3.8	-2.0	79.3	85.8	70.8	54.3
S5-6a	-	-	-6.8	-1.3	-	-	-52.4	-28.2
S6a-6b	-	-	-31.5	-38.0	-	-	-	-
S6-7	52.7	58.8	18.4	10.8	42.5	17.2	-31.1	-53.8

Supplementary Table 5. Calculated free energy (G) and enthalpy (H) changes for reaction (ΔX_{react}) and activation (ΔX_{act}) steps at 350 K, covering all elementary steps of propene hydroformylation within the periodic MFI model. All energies are given in kJ/mol.

Step	Rh^+				Rh^{3+}			
	ΔG_{act}		ΔG_{react}		ΔG_{act}		ΔG_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	25	19.5	-	-	33.5	27.5
S2-3	2.9	2.6	-27.8	-8.2	-	-	-	-
S3-4	-	-	-95.2	-64.6	-	-	-151.3	-179.6
S4-5	58.8	50.1	33.3	28.9	77.9	148.8	37.8	72.8
S5-6	-	-	16.5	8.3	-	-	-31.6	32.3
S6-7	23.6	15.6	-51.4	-51.7	92.3	56.6	9.8	-5.6
	ΔH_{act}		ΔH_{react}		ΔH_{act}		ΔH_{react}	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	25.4	20.3	-	-	34.3	30.7
S2-3	3.7	1.1	-29.3	-11.1	-	-	-	-
S3-4	-	-	-111.5	-80.9	-	-	-169.0	-199.0
S4-5	55.2	46	26.3	25	75.2	145.7	36.8	71.0
S5-6	-	-	-11.6	-26.7	-	-	-67.2	-2.1
S6-7	19.9	19.1	-62.5	-46.7	91.6	59.8	12.3	-4.3

2) The authors have clarified the mechanism; the Reviewer thinks it is important to highlight in the main text the change of reaction mechanism with Rh(III) intermediates; favoring sigma-bond metathesis over oxidative addition (as observed for Rh(I); this will be particularly valuable for the readers in molecular chemistry, which may decide to design novel systems based on this work.

Response: We thank the Reviewer for the suggestion. We agree that explicitly highlighting the mechanistic divergence between Rh^+ and Rh^{3+} intermediates is important for readers as it emphasizes the change from oxidative addition-reductive elimination to σ -bond metathesis-type reactivity.

In response, we have incorporated the following paragraph in the manuscript of Page 8 to clarify that this is an important mechanistic distinction between the two studied active sites models:

“Finally, there is a key mechanistic difference between Rh^+ and Rh^{3+} pathways. Up to acyl formation, the mechanisms are analogous. However, subsequent steps differ from the classical oxidative addition-reductive elimination accepted for Rh^+ . Instead, for Rh^{3+} the mechanism proceeds via H_2 adsorption followed by aldehyde formation through a σ -bond metathesis-type step, such that the formal oxidation state of rhodium remains +3 throughout the catalytic cycle. Furthermore, H_2 adsorption is exergonic for the linear pathway but endergonic for the branched pathway (Figure 2), with this difference arising mainly from the enthalpic contribution (Table S5). The complete mechanism is detailed in the Supporting Information, Section 2.11”

Given the space constraints imposed by the journal format, the discussion is necessarily kept concise in the main text. However, the Supporting Information provides a more detailed mechanistic description.

3) Based on the answer of the authors; the reviewer was puzzled by the assignment of some of the Rh(CO) surface sites to Rh(II) species, while it is not discussed (and evaluated) in the XANES section. This needs to be clarified why it is not included in

the XANES analysis if it is inferred according to IR. Any other interpretation? Any other evidence for Rh(II), like EPR?

Response: We thank the reviewer for highlighting this apparent discrepancy.

The initial K₂RhCl₆@MFI-Cal sample contains some Rh²⁺ species before reaction (2121 cm⁻¹). However, after the hydroformylation reaction, only Rh³⁺ and Rh⁺ species are observed in both the spent K₂RhCl₆@MFI-Cal and K₂RhCl₆@MFI-Cal-500MP catalysts, indicating that the initial Rh²⁺ species are transformed under the reaction conditions. (see Figure R6a and b).

Furthermore, as suggested by the referee we did EPR studies to analyze the presence of Rh²⁺ in the fresh sample (See Figure R7). In the fresh sample a signal of $g = 2.14$ is observed which could be assigned to Rh²⁺ species⁹, in consistence with the IR data described above.

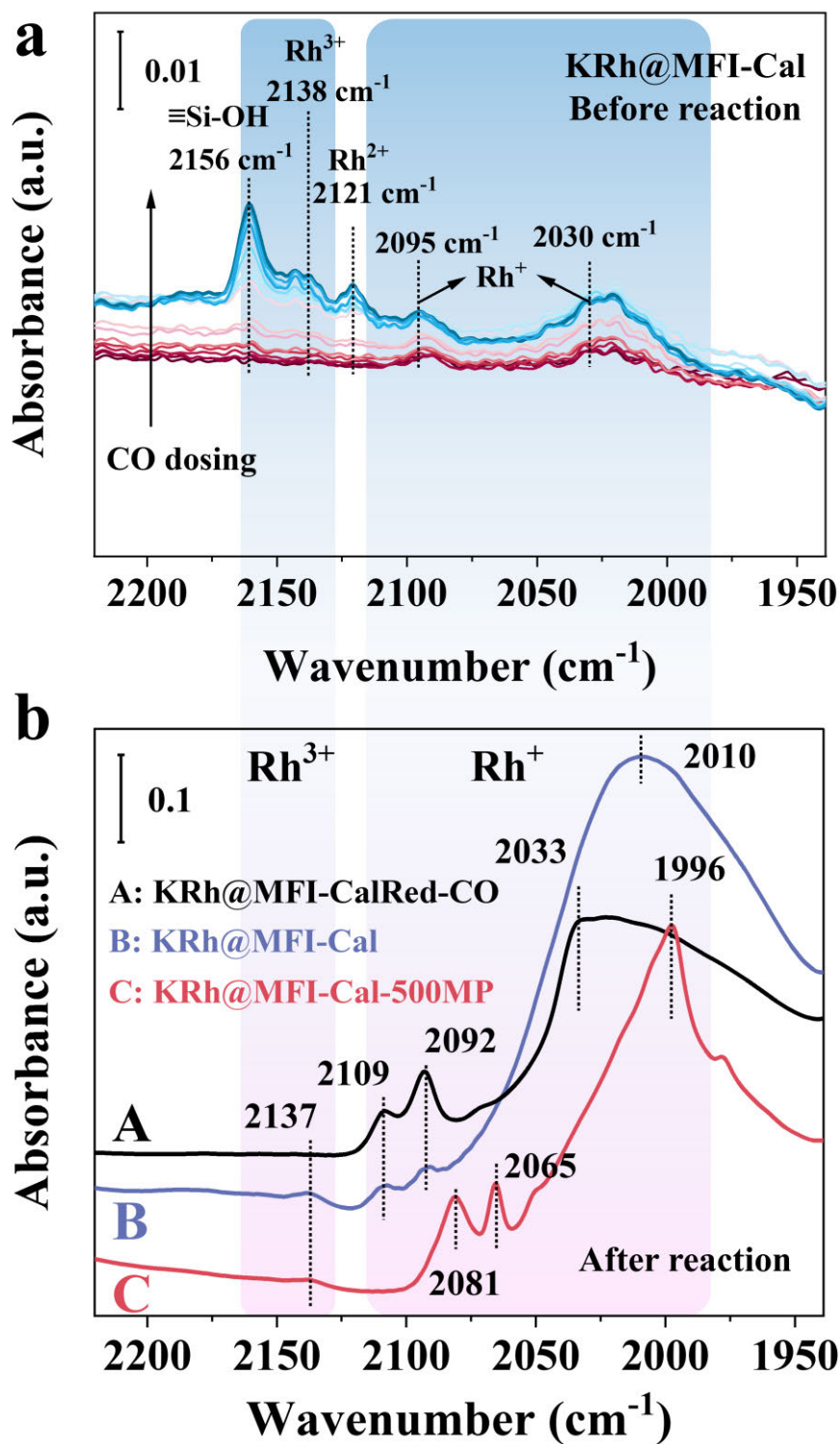


Figure R6. (a) IR-CO spectra for KRh@MFI-Cal before reaction (0-2 mbar), KRh@MFI-CalRed-CO (2 mbar), KRh@MFI-Cal after 1-hexene hydroformylation reaction (2 mbar), and KRh@MFI-Cal-500MP after 1-hexene hydroformylation reaction (2 mbar) at $-65\text{ }^{\circ}\text{C}$.

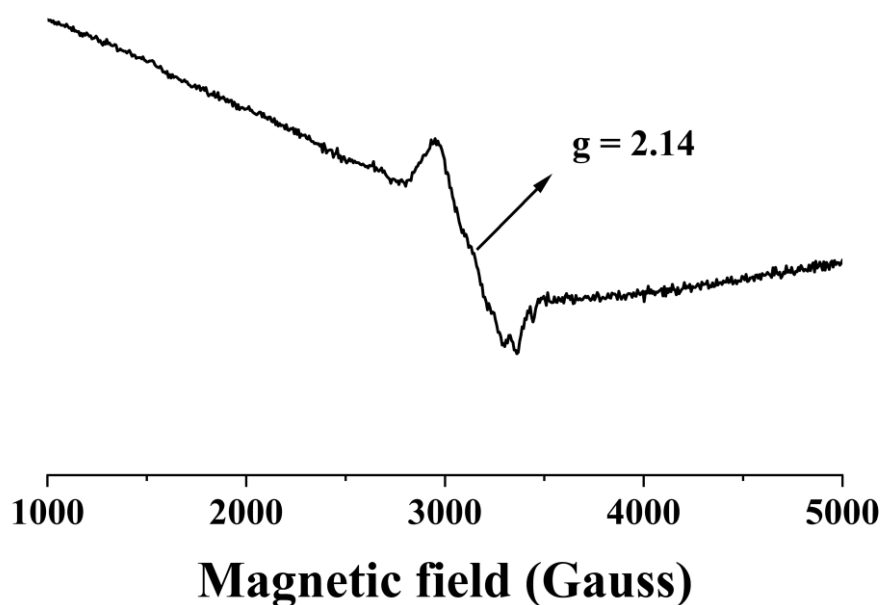


Figure R7. EPR result of KRh@MFI-Cal sample at 100K.

4) In addition the IR signatures of few (some fully characterized) Rh(III) carbonyl have been discussed in the literature, e.g. New J. Chem., 2024, 48, 18365-18375; Inorg. Chem. 2003, 42, 3801-3814; JOMC 1979, 165, 93. Their IR signatures seem to be close in some cases to the Rh(II) species discussed above. Some would be nice references for XANES. The authors should consider these references to further support their interpretation.

Response: We thank the reviewer for the valuable comment and for bringing these informative references to our attention. We have carefully checked the information provide in these references and compared in Figure R8. As indicated, the CO stretching frequencies of Rh(I) carbonyl species are typically observed below 2100 cm^{-1} , whereas Rh(III) carbonyl species generally exhibit significantly higher frequencies ($>2100\text{ cm}^{-1}$, and in some cases even exceeding 2200 cm^{-1}). This trend is well established and originates from the higher oxidation state of Rh(III), which possesses a lower electron density and therefore exhibits much weaker metal-to-CO π -back donation. The reduced back-donation strengthens the C-O bond, resulting in a higher CO stretching frequency. Besides, it should be noted that the CO stretching frequency of Rh(I) or Rh(III) carbonyls are also strongly influenced by the surrounding ligands, which reflects on

unusual vibrational frequencies reported in above reference (e.g. Inorg. Chem. 2003, 42, 3801-3814). Notice that all these references correspond to homogeneous Rh(I) and Rh(III) carbonyl complexes with different organic ligands or only bulk compounds, whose CO vibration frequencies may differ to that observed in heterogeneous systems.

To get a more reliable assignment of the observed IR bands, we have comprehensively summarized in Table R5 the state-of-the-art literature on heterogeneous catalyst with Rh carbonyl species supported on zeolites and metal oxides, including the characteristic CO stretching frequencies of gem-dicarbonyls, linear carbonyls, and bridged carbonyls. We believe that this compilation provides a more systematic basis for distinguishing Rh^+ , Rh^{3+} , and metallic Rh species.

Based on the state-of-the-art IR-CO assignments summarized in Table R5, the CO stretching band of Rh^{2+} is typically observed at around 2120 cm^{-1} , whereas that of Rh^{3+} appears in the $2135\text{-}2145\text{ cm}^{-1}$ region. This is consistent with our interpretation. Since no Rh^{2+} species were detected in the IR-CO measurements of those samples after reaction (Figure R6b), the contribution of Rh^{2+} to the observed IR-CO spectra can reasonably be considered negligible.

We have updated Table R5 in the Supporting Information as Supplementary Table 24 in section “**Appendix 3.7. Summary of the identification of Rh species by IR-CO**”. The most relevant references supporting the assignment of the different Rh species have also been updated in the manuscript.

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Table R5. Vibrational frequencies of gem-dicarbonyls, linear carbonyls, and bridged carbonyls of rhodium supported on zeolites and metal oxides.

Initial forms of catalyst	Pre-treatment	Temperature of IR-CO (°C)	O-RhCO		ν_s Rh(CO) ₂	ν_{as} Rh(CO) ₂	RhCO	Rh ₂ CO	Ref
			Rh ³⁺	Rh ²⁺	Rh ⁺	Rh ⁺	Rh ⁰	Rh ⁰	
Supported molecular Rh complex									
Rh(C ₂ H ₄) ₂ /H-Beta	None	25			2115	2048			10
Rh(CO) ₂ /DAY zeolite	None	25			2116	2050			11
Rh(C ₂ H ₄) ₂ /SAPO 37	None	25			2115	2052			12
Rh(CO) ₂ /ZSM-5	None	25			2116	2049			13
Rh(C ₂ H ₄) ₂ /HY	None	25			2118	2052			10
RhCl ₃ ·3H ₂ O/Al ₂ O ₃	None	25	2135		2088	2016			14
Rh ₆ (CO) ₁₆ /Al ₂ O ₃	CO, 25 °C	25			2095	2020			14
Rh ₆ (CO) ₁₆ /Al ₂ O ₃	O ₂ , 200 °C	200	2135						14
Rh ₆ (CO) ₁₆ /Al ₂ O ₃	CO, 100 °C	100			2095	2020			14
RhCl ₃ /SiO ₂	He, 30 °C	30	2145		2102	2036			15
RhCl ₃ ·3H ₂ O/Al ₂ O ₃	Vacuum	25	2136		2098	2029			16
RhCl ₃ ·3H ₂ O/Al ₂ O ₃	H ₂ , 150-400 °C	25			2096-2102	2022-2032	2042-2076	1845-1875	16
Supported Rh nanoparticles/clusters/atoms									
Rh/Al ₂ O ₃	H ₂ 500 °C, then O ₂ 27 °C	27		2128	2110	2038			17
Rh/NaY			2138						18
Rh/HY	H ₂ , 300 °C	50			2114, 2100	2049, 2025	1990	1843	19
Rh/KY	H ₂ , 300 °C	50			2109, 2092	2042, 2014	1999	1812	19
Rh/SiO ₂	H ₂ , 350 °C	25					2067	1901	20
Rh/Al ₂ O ₃	H ₂ , 250 °C	23		2120	2091	2020		1810-1835	21
Rh/Al ₂ O ₃	H ₂ , 100 °C		2142	2120	2090	2017			22
Rh/SiO ₂	H ₂ , 200 °C	25			2104	2042	2048-2067	1900-1925	23
Rh/DAY zeolite	Air, 400 °C	25			2118	2053			24
	H ₂ , 300 °C	25			2093	2036	2075	1860	24
Rh/Na-Y zeolite	CO, 100 °C	25			2086	2010			25
Rh/TiO ₂	H ₂ , 200 °C	−120			2097	2031			26
	H ₂ , 300 °C	−120			2094	2030	2070		26
	H ₂ , 300 °C	25			2094	2027			26
Rh/DeAl-Beta	H ₂ , 200 °C	30			2093-2113	2037-2048	2069	1915	3
RhZn/DeAl-Beta	H ₂ , 200 °C	30			2096	2030	2066		3
RhCo/DeAl-Beta	H ₂ , 200 °C	30			2096	2025	2064		3

5) Minor comments: The Reviewer feels that the quality of the Figures could be improved; most figures look a bit crude considering what can be done nowadays with computer graphics.

Response: We thank the reviewer for the valuable comment. We agree that the visual presentation of the figures can be further improved. Accordingly, we have carefully revised the figures by improving the layout, font consistency, line thickness, color scheme, and overall graphical presentation to enhance their clarity and professional appearance. In addition, all original figures were prepared at high resolution (≥ 300 dpi), and we will provide the original high-resolution files to ensure optimal reproduction during the publication process.

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The authors appreciate the referee's effort and time for the critical review of the manuscript again. The manuscript has been updated with new information and a point-to-point answer to all the comments risen by the referees is included in this document in red color.

Referee #1

Comments:

The authors have improved the paper according to the review comments. I believe this work constitutes a significant contribution to hydroformylation catalysis, and therefore, I recommend its publication in Nature.

Response: We appreciate all the suggestions made by the referee that would be very helpful for improving the quality of the manuscript. We also thanked the referee for the positive and encouraging evaluation along the process.

Referee #2

Comments:

The authors have improved the manuscript, which is probably suitable for publications.

See below some minor comments and corrections.

1) The authors used the term H₂ adsorption, while it is probably better to use the term H₂ coordination.

Response: We agree with the referee that the term “H₂ coordination” is more appropriate than “H₂ adsorption” in the context of our study. We have therefore replaced “H₂ adsorption” with “H₂ coordination” throughout the manuscript and Supporting Information.

2) In ESI, the Tables with enthalpies and Gibbs free energies are presented in a sub-optimal way as it is difficult to easily assess the impact of entropy. The two tables could be merged with Gibbs free energy and Enthalpy values provided side by side, for instance as follows; Delta G (Delta H) for each step and TS as it allows to directly assess the impact of entropy without the need to look at two Tables. Also providing both values in (the) a Figure (potential energy surface) would be helpful

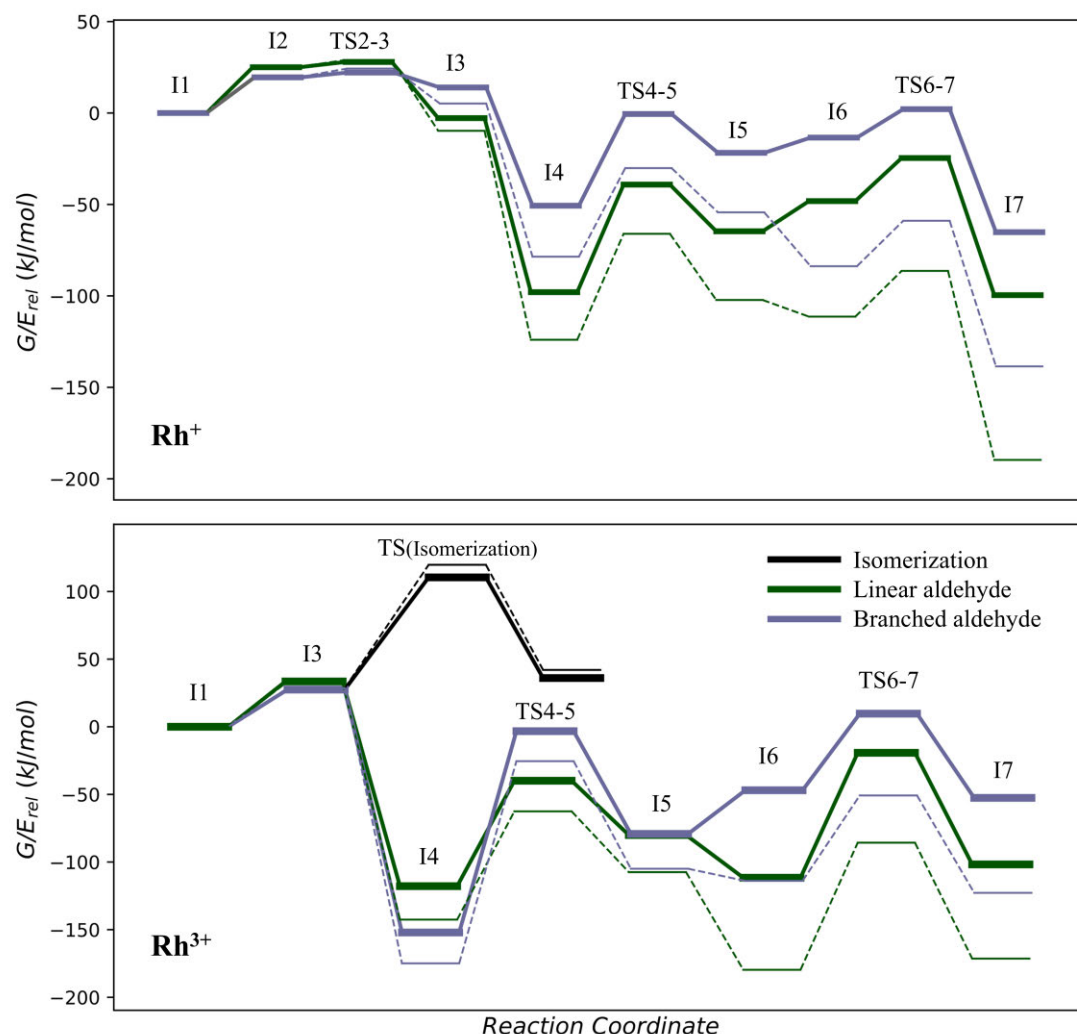
Response: Following the referee’s suggestion, we have modified **Supplementary Table 4** and **Supplementary Table 5** in the Supporting Information to present the enthalpy and Gibbs free energy values side by side, allowing the contribution of entropy to be assessed more directly for each step. In addition, we have revised the energy profile in **Supplementary Fig. 24** to include the potential energy values, represented by dashed lines, together with the corresponding free energy values.

Supplementary Table 4. Calculated free energy (G) and enthalpy (H) changes for reaction (ΔX_{react}) and activation (ΔX_{act}) steps at 300 K, covering all elementary steps of propene hydroformylation with the isolated complex models $\text{RhH}(\text{CO})_2(\text{PH}_3)_2$ and $\text{RhH}(\text{OH})_2(\text{PH}_3)_2$. All energies are given in kJ/mol.

Step	Rh^+				Rh^{3+}			
	$\Delta G_{\text{act}} (\Delta H_{\text{act}})$		$\Delta G_{\text{react}} (\Delta H_{\text{react}})$		$\Delta G_{\text{act}} (\Delta H_{\text{act}})$		$\Delta G_{\text{react}} (\Delta H_{\text{react}})$	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	46.8 (37.3)		-	-	41.5 (34.9)	42 (34.2)
S2-3	48.9 (56.2)	56.4 (62.7)	0.4 (5.0)	5.4 (8.8)	4.6 (8.4)	8.0 (13.1)	-0.4 (-1.5)	-1.3 (-0.4)
S3-4	-	-	-43 (-91.6)	-53.1 (-99.6)	-	-	-97.2 (-144)	-83.8 (-131.5)
S4-5	49.7 (57.5)	71.6 (75.4)	-4.18 (-3.8)	-2.5 (-2.0)	72.1 (79.3)	80.4 (85.8)	60 (70.8)	46 (54.3)
S5-6a	-	-	31 (-6.8)	36.8 (-1.3)	-	-	-10.1 (-52.4)	11.3 (-28.2)
S6a-6b	-	-	-29.7 (-31.5)	-35.9 (-38.0)	-	-	-	-
S6-7	44.7 (52.7)	53.4 (58.8)	1.7 (18.4)	-3.3 (10.8)	40.6 (42.5)	15.9 (17.2)	-30.6 (-31.1)	-55.2 (-53.8)

Supplementary Table 5. Calculated free energy (G) and enthalpy (H) changes for reaction (ΔX_{react}) and activation (ΔX_{act}) steps at 350 K, covering all elementary steps of propene hydroformylation within the periodic MFI model. All energies are given in kJ/mol.

Step	Rh⁺				Rh³⁺			
	ΔG_{act} (ΔH_{act})		ΔG_{react} (ΔH_{react})		ΔG_{act} (ΔH_{act})		ΔG_{react} (ΔH_{react})	
	PL	PB	PL	PB	PL	PB	PL	PB
S1-2	-	-	25 (25.4)	19.5 (20.3)	-	-	33.5 (34.3)	27.5 (30.7)
S2-3	2.9 (3.7)	2.6 (1.1)	-27.8 (-29.3)	-8.2 (-11.1)	-	-	-	-
S3-4	-	-	-95.2 (-111.5)	-64.6 (-80.9)	-	-	-151.3 (-169.0)	-179.6 (-199.0)
S4-5	58.8 (55.2)	50.1 (46.0)	33.3 (26.3)	28.9 (25.0)	77.9 (75.2)	148.8 (145.7)	37.8 (36.8)	72.8 (71.0)
S5-6	-	-	16.5 (-11.6)	8.3 (-26.7)	-	-	-31.6 (-67.2)	32.3 (-2.1)
S6-7	23.6 (19.9)	15.6 (19.1)	-51.4 (-62.5)	-51.7 (-46.7)	92.3 (91.6)	56.6 (59.8)	9.8 (12.3)	-5.6 (-4.3)



Supplementary Fig. 24. Energy profiles. Free energy (solid line) and energy (dashed line) profiles of hydroformylation on Rh⁺ (upper panel) leading to the formation of *n*-butanal (green) and methylpropanal (violet), and on Rh³⁺ (lower panel) for *n*-butanal (green) and methylpropanal (violet) and isomerized alkene (black), within the periodic MFI model.

3) As pointed out in my previous report, the Schemes and Figures could be improved (e.g. the use of times or related font for Scheme and to draw molecules is often not ideal); it is a matter of taste and policies but anything making figures appealing is a plus.

Response: We thank the reviewer for this suggestion. In accordance to Nature's formatting guidelines, we have revised all text appearing in the Figures to Arial font. Furthermore, following the editor's suggestion, we have simplified Fig. 4 to improve its clarity and readability. We have also rearranged the schematic in Extended Data Fig.

1 to present the information in a more logical and clearer manner. We believe that some descriptive text is necessary to facilitate readers' understanding and have therefore kept these explanatory descriptions.

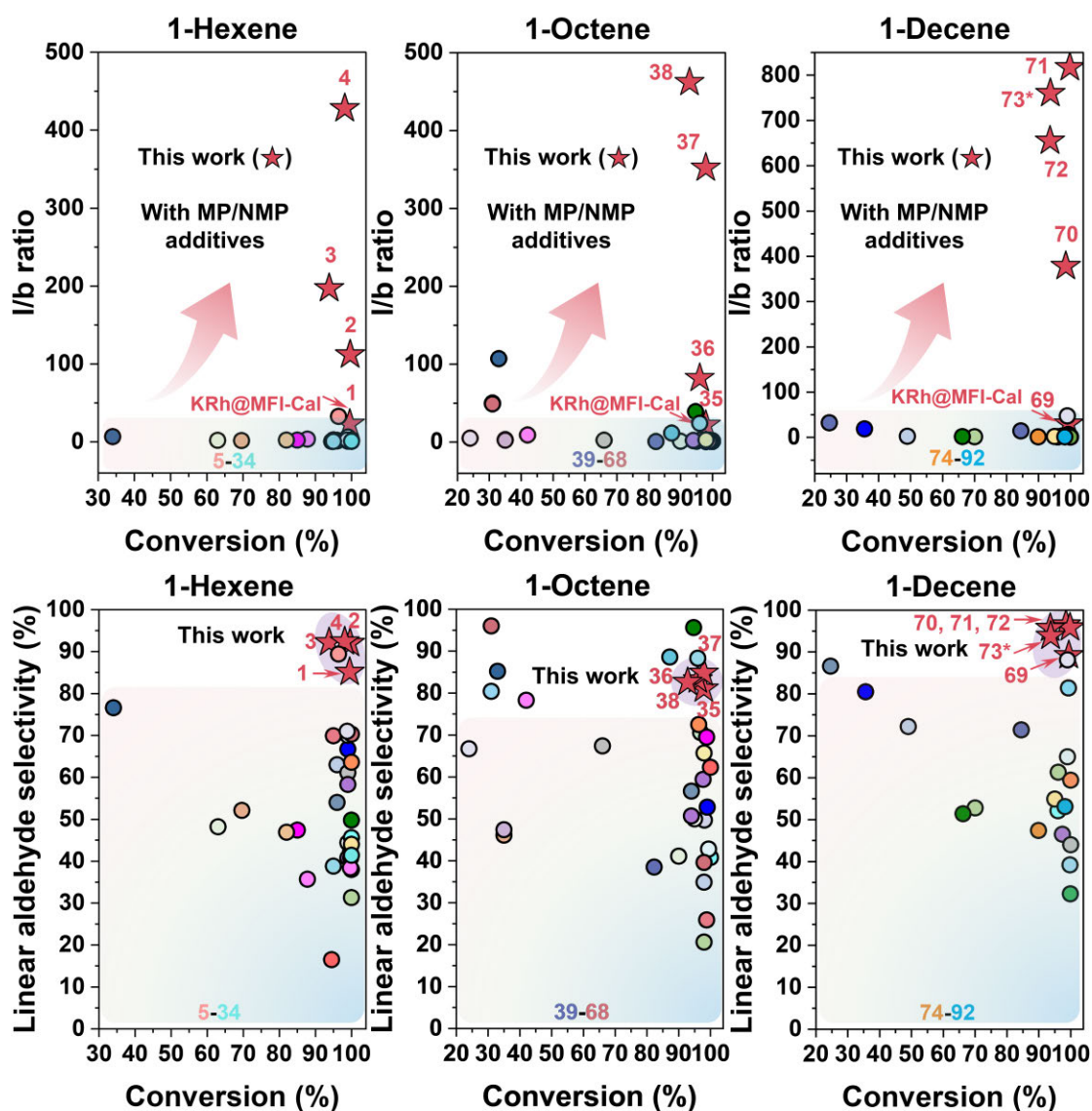
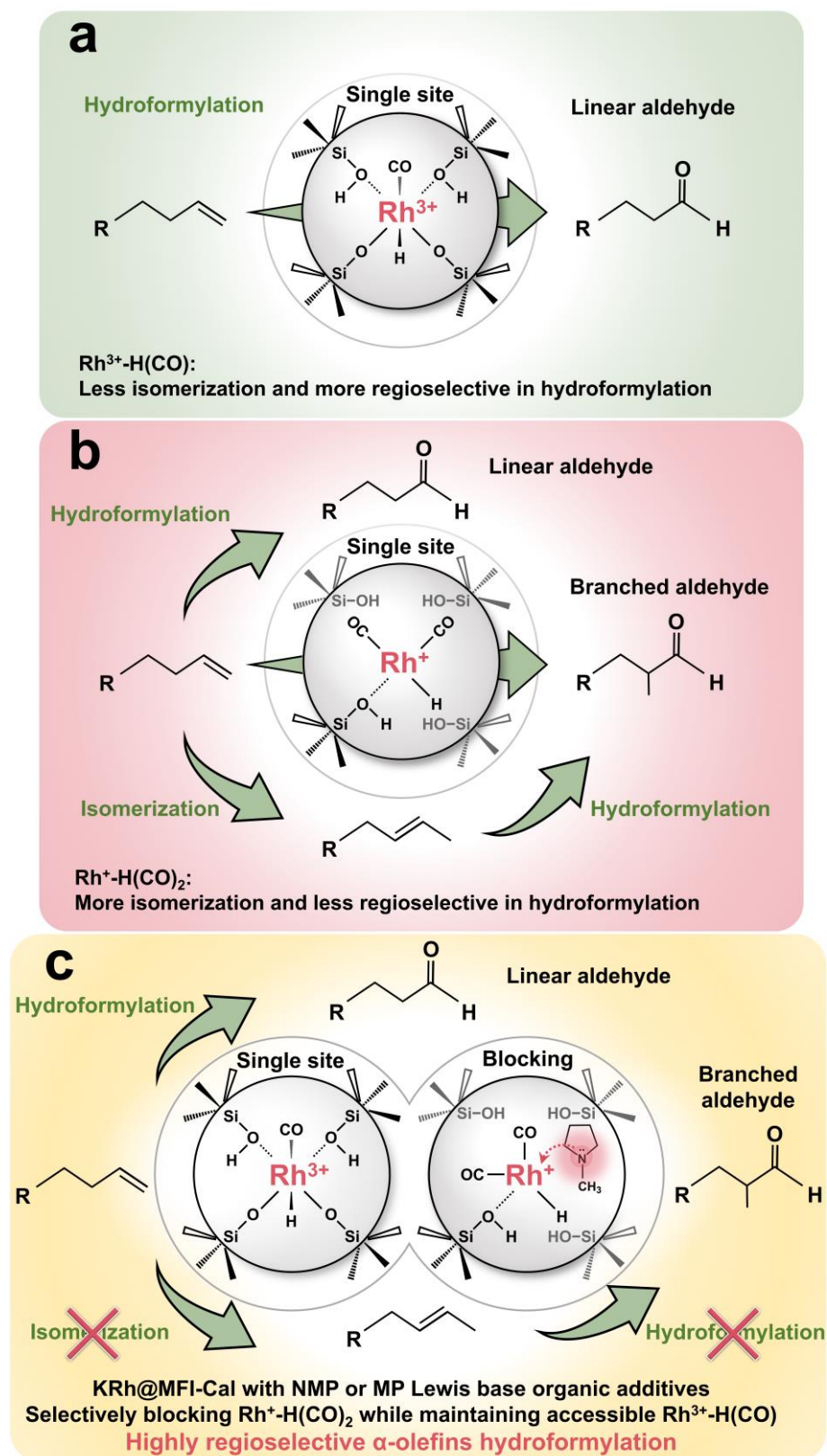


Fig. 4 | State-of-the-art C6-C10 α -olefins hydroformylation. Comparison of the catalytic performance of KRh@MFI-Cal and with MP/NMP organic additives with state-of-the-art heterogeneous and homogeneous catalysts (Numbers correspond to the entries of Supplementary Table 13 in the Supplementary Information).



Extended Data Fig. 1 | Schematic illustration of α -olefins hydroformylation. a, $\text{Rh}^{3+}\text{-H(CO)}$ active site, b, $\text{Rh}^+\text{-H(CO)}_2$ active site, c, NMP or MP blocked $\text{Rh}^+\text{-H(CO)}_2$ active site.