



Leaching of palladium atoms from small cluster models during Heck reactions – An experimental and theoretical study

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ARTICLE INFO

Keywords:

Palladium leaching
Heck reaction
DFT calculations
Solid-liquid interface

ABSTRACT

Relevant parameters for the leaching of palladium atoms from small Pd clusters during Heck reactions of bromobenzene and styrene have been explored computationally and experimentally. With density functional theory calculations, we modeled reaction free energies for removing a Pd atom from a Pd₆ model cluster and for forming Pd-ligand complexes. Oxidative addition of bromobenzene decreases the dissolution energy. Additional parameters and mechanisms, especially bromide ions render the leaching process notably exergonic. Model results exhibit the same trends as the targeted experiments where Pd leaching from supported catalysts (Pd/C, Pd/SiO₂) was monitored as function of reaction temperature, time and components.

1. Introduction

All heterogeneously catalyzed reactions in liquid phase are potentially associated with the question of partial dissolution or leaching phenomena. Leaching of the active metal into the liquid reaction mixture may cause a loss in catalytic activity and lead to contaminated products. In specific reactions, dissolution of active metal species can also result in an even more efficient homogeneous catalytic cycle with increased reaction rates. This has been observed for palladium catalyzed C–C coupling reactions of Heck- [1] and Suzuki-type. [2] For these reactions, a variety of authors did not regard leaching primarily as a negative phenomenon, but proposed Pd leaching as a prerequisite for high catalytic activity. [3–7] However, several studies also reported that Heck and in particular Suzuki coupling reactions occur at the surface of solid Pd as truly heterogeneous reaction with a classical surface mechanism; for a review see Ref. [8]. While leaching of Pd into solution (and re-deposition) has been proven in many experiments, relevant parameters and mechanisms of leaching remain often unclear in detail.

Especially in the case of Heck reactions, the matter of how the reaction is catalyzed starting from solid Pd drew much attention. Several contributions and reviews addressed this topic [7–11], proposing in

particular the generation of active species in solution through oxidative addition of the aryl halide to Pd particles. [8] Ananikov et al. discussed the simultaneous existence of several active species in solution (dissolved palladium complexes, clusters and nanoparticles etc.) and their interconversions as a “cocktail of catalysts”. [12] De Vries examined the catalytic relevance of the formation of palladium colloids and anionic palladium species in solution at higher temperatures. [7] In several experiments, the rate of conversion correlated with the concentration of dissolved palladium species. [4,13,14] Analogous concepts of palladium leaching exist for Suzuki-Miyaura type cross-coupling reactions. [15–17] The catalysts and reaction mixtures were monitored in situ during the Heck reaction by means of EXAFS by Kleist et al. [18] showing that the catalyst changed from solid to dissolved species as the substrate is converted. Analogous observations were reported in NMR studies by Smirnov [19] and with a nanoporous membrane reactor by Gaikwad et al. [20]

A detailed understanding of how potential elementary steps may contribute to palladium leaching during carbon-carbon coupling reactions was obtained by theoretical studies of Polynski and Ananikov [21], Ramezani-Dakhel [22], Proutiere [23], and Chang et al. [24] The DFT investigations report the dissolution into the liquid phase, e.g. as

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<https://doi.org/10.1016/j.catcom.2022.106441>

Received 31 December 2021; Received in revised form 28 February 2022; Accepted 2 March 2022

Available online 4 March 2022

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function of the palladium particle size as well as the possibility of Pd leaching from solid Pd surfaces into the gaseous phase by means of CO chemisorption. A review of theoretical studies on aspects of carbon-carbon bond formation has been published by Xue and Lin 2010. [25]

With the work presented here, we intended to examine specific parameters of such leaching processes by close correlation of targeted experiments with computational model results. Leaching processes at solid-liquid interfaces are very complex as they involve solid surfaces, solvent, substrates and additives. It seems reasonable to reduce the complexity by addressing selected parameters and elementary steps. The computational work focuses on the thermodynamics of the leaching process, i.e. which Pd species is most likely to dissolve and energetically stabilized in solution. We address the questions (i) which reaction parameters (components) favor palladium leaching and (ii) under which reaction conditions leaching may be preferably observed. Temperature-programmed experiments correlating dissolved palladium and catalytic activity on the one hand side and experiments with variation of reactant composition (optional with and without aryl halide, alkene, additional bromide ions) - again as function of temperature and time - were carried out for these reasons. The study addresses the role of all individual components of typical Heck reactions under so-called Jeffery conditions [26], emphasizing bromide ligands.

2. Results and discussion

2.1. Leaching under standard Heck reaction conditions

We started our study with experiments on how the amount of dissolved palladium correlates with the rate of substrate conversion as described before. [27] In this first experiment with the complete Heck reaction mixture (Scheme 1) the leaching characteristics are analogous to previous studies on leaching in Heck reactions. [6]

The conversion of bromobenzene, PhBr (blue “x” in Fig. 1), starts at a temperature of about 140 °C, the typical temperature for converting aryl bromides in Heck reactions. The “leaching curve” (full circles, green) shows the amount of palladium determined in samples taken from the reaction mixture, while still being hot, applying filtration by a 200 nm syringe filter. Palladium determination was conducted by elemental (trace) analysis (see Experimental).

The graphs are characterized by the coincidence of the maximum rate of conversion (indicated by the inflection point in the conversion curve) and the maximum of the leaching curve. Catalytically active species are formed by metal leaching from the solid catalyst, undergoing catalytic cycles and redeposited (as Pd metal particles, XRD, TEM, see [6]) when the substrate is consumed.

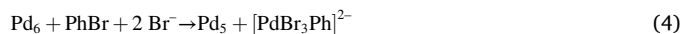
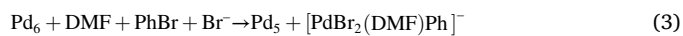
The most common interpretation of Pd dissolution in the literature is that oxidative addition of PhBr causes formation of dissolved molecular palladium species. The question arises however which other parameters and mechanisms contribute to leaching and to which extent. DFT calculations presented in the following shall examine how plausible such assumptions are, by exploring the energetics of this and related processes resorting to simple model system. The results of these calculations led to the targeted leaching experiments, Section 2.3.

2.2. DFT modeling

To assess which parameters support leaching of palladium from a

solid particle, a simple model has been created based on the comparison of relative energies simulated by DFT calculations of solid and dissolved states. In detail, we chose the octahedral cluster Pd_n, n = 6, as model, and compared the overall energetic situation after detaching (“leaching”) one Pd atom, see Fig. 2.

The final state, a cluster Pd_{n-1} and a coordinated Pd atom, are not strongly dependent on the cluster size, such that this small model seems sufficient for exploring energy trends of the following formal transformations:

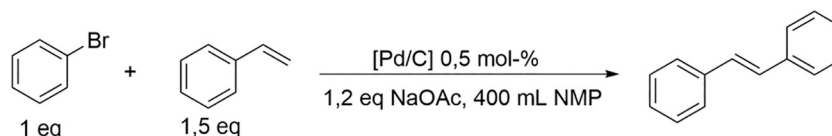


The free energy including solvation corrections was calculated for forming of a Pd complex with various ligands according to Eqs. (1) to (4). Eq. (1) is taken as simple model procedure where one palladium atom is abstracted from the original cluster Pd₆ by forming the tetrakisdimethyl formamide (DMF) complex. In Eq. (2) we considered the oxidative addition by introducing PhBr, forming the complex [PdBr(DMF)₂Ph]. In Eqs. (3) and (4), we modeled the effect of additional bromide ions, which occur under Jeffery conditions [26], but in our modeling strategy are taken to describe the consequences of several catalytic cycles. The DFT calculations were carried out in all-electron scalar relativistic (spin-unrestricted) fashion using the revised PBE GGA exchange-correlation functional. For further details, see below the Section “Computational”.

Comparing the calculated free reaction energies G_r of reactions 1–4 (Table 1), we note from our model results that the solvent alone (DMF) is not able to support Pd leaching, as reflected by the rather high positive reaction free energy, Eq. (1). Addition of PhBr remarkably decreases the reaction free energy to about 170 kJ/mol, Eq. (2), indicating that the presence of PhBr plays a crucial, beneficial role in the leaching step. The energy trends agree very well with the conclusions from experiments and theory [21–23] that the oxidative addition of aryl halides plays an important role in palladium leaching. Addition of another bromide ion, Eq. (3), in our model system entails a further strong reduction of G_r by 150 kJ/mol. Finally, Eq. (4), the third bromide ion has a smaller effect, as G_r is reduced by ~80 kJ/mol, rendering the leaching energetically favorable, even in our model system. According to these G_r values obtained for oxidative addition and bromide coordination, dissolution of a palladium atom as complex is thermodynamically feasible especially for the most stable Pd complex containing several Br⁻ ligands.

2.3. Leaching experiments under Heck conditions at varying temperatures omitting one or more components

Our model calculations suggest a favorable thermodynamic effect due to the presence of bromide ions. Thus, the question arises: what happens if bromide ions are present in the reaction solution, but no aryl halide? Using a top-down approach in close connection with the computed data, we thus systematically reduced the number of components and tested experimentally if leaching (as in Fig. 1) was still observable. This approach had already been followed in other reports [28], yet without monitoring leaching temperature and time. The



Scheme 1. Reaction equation and reaction conditions of the Heck coupling investigated.

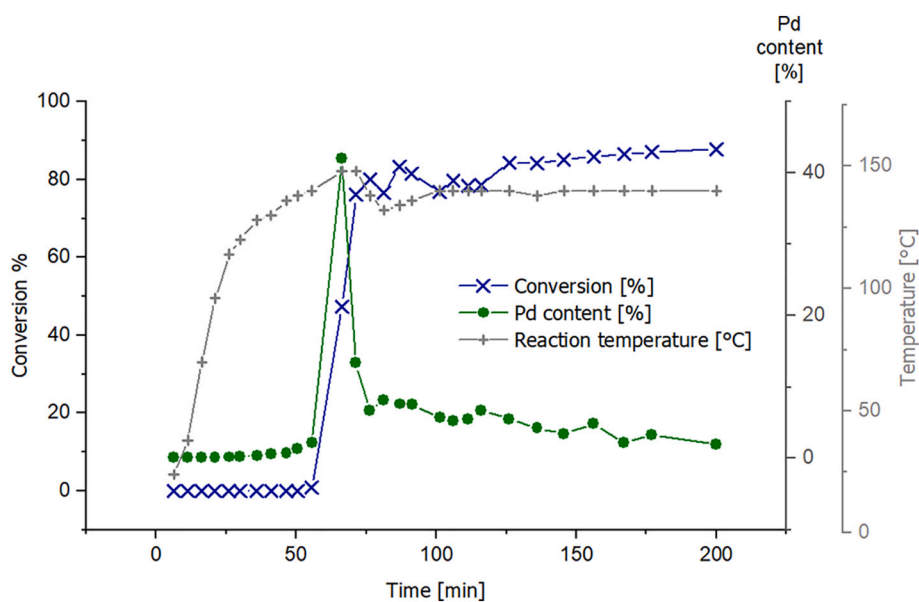


Fig. 1. Leaching under standard Heck reaction conditions as bromobenzene is converted with styrene as a function of reaction time (full circles, green): leached Pd in % of total Pd; crosses (x, blue): conversion of bromobenzene in % (selectivity to coupling product: > 95%); “+”, grey: temperature profile in °C; reaction conditions: 1 eq bromobenzene, 1,5 eq styrene, Pd 0,5 mol-%, 1,2 eq sodium acetate in *N*-methyl-2-pyrrolidone (NMP), max. temp. 140 °C, 3 h; catalyst: Pd/activated carbon (5 wt.-%); for detailed values of Pd in solution see SI, Table S1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

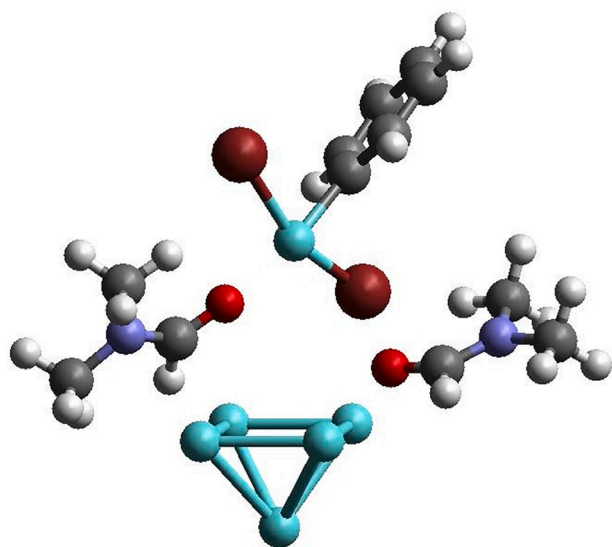


Fig. 2. Computational model system where one palladium atom of a Pd₆ cluster (cyan) is taken to interact with the reaction environment, forming a Pd₅ cluster and a [PdPh(Br)₂(DMF)₂] complex illustrating the theoretical approach (bromide: red, carbon: grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Reaction free energies G_r for dissolving one palladium atom as a complex from a Pd₆ cluster with various ligand configurations from DFT model calculations.

Reaction	G_r (150 °C, 1 bar) kJ/mol
$\text{Pd}_6 + 4 \text{ DMF} \rightarrow \text{Pd}_5 + [\text{Pd}(\text{DMF})_4]$	517
$\text{Pd}_6 + 2 \text{ DMF} + \text{PhBr} \rightarrow \text{Pd}_5 + [\text{PdBr}(\text{DMF})_2\text{Ph}]$	165
$\text{Pd}_6 + \text{DMF} + \text{PhBr} + \text{Br}^- \rightarrow \text{Pd}_5 + [\text{PdBr}_2(\text{DMF})\text{Ph}]^-$	14
$\text{Pd}_6 + \text{PhBr} + 2 \text{ Br}^- \rightarrow \text{Pd}_5 + [\text{PdBr}_3\text{Ph}]^{2-}$	-69

reaction plan for this is summarized in Table 2. Apart from the variation of the reaction composition, the concentration of palladium in solution was monitored in short time intervals and with increasing temperature comparable to experiments with all reaction components present in Fig. 1 (temperature-programmed leaching study). All experiments were

Table 2

Survey on the reaction conditions of systematic leaching experiments n (TBAB: tetrabutylammonium bromide.; NMP: *N*-methylpyrrolidone).

	n	bromobenzene	styrene	TBAB	NMP
Full Heck conditions (Fig. 1)	0	X	X	X	X
Reduced Heck conditions	1	X			X
	2			X	X
	3	X		X	X
	4		X		

repeated with Pd/activated carbon (5 wt.-%) as well as with Pd/SiO₂ (1 wt.-%) to ensure reproducibility and to achieve a higher generalizability of conclusions.

The experimental results are shown in Fig. 3 for palladium supported on activated carbon, Pd/C (5 wt.-%). According to the hypothesis derived from previous studies and theoretical results, leaching should also occur if styrene is not present in the reaction mixture. This experiment with bromobenzene (250 mmol), 0.5 mol-% palladium with respect to bromobenzene and *N*-methylpyrrolidone (NMP, 250 mL) as standard solvent corresponds to Eq. (2). The leaching curve (+, black) shows the percentage of total Pd, which has been leached into solution at the temperature given (about 2%). In fact, Pd is leached with PhBr and NMP at temperatures equal to and higher than 120 °C with a maximum at 130 °C, i.e., the temperature at which the Heck reaction (oxidative addition as assumed rate determining step) started (Fig. 1). At higher temperature and increased reaction time, dissolved Pd is (at least partially) re-deposited (Pd concentration reduced). This can be interpreted as effect of reduction of Pd(II) – the oxidation state of Pd after dissolution - and missing stabilizing ligands. In analogous experiments with water and NMP only (not shown), leaching was not detected at all.

In exp. 2 of Table 2, only tetrabutylammonium bromide (TBAB) (5 mmol) and solvent NMP (130 mL) were reacted with supported Pd. TBAB is considered as source for bromide ions and well-soluble in the reaction mixture. Dissolution of palladium occurred even at lower temperature (clearly below 100 °C) and to larger extent (up to >5% of the total Pd/C). This underlines the driving force of palladium bromido complex formation as predicted by our model calculations and the oxidation state Pd(II). Again, a maximum is observed with analogous interpretation to experiment $n = 1$. Exp. 3 (Table 2) was carried out with bromobenzene, TBAB and NMP. In agreement with expectations and model calculations, leaching already starts at lower temperature and

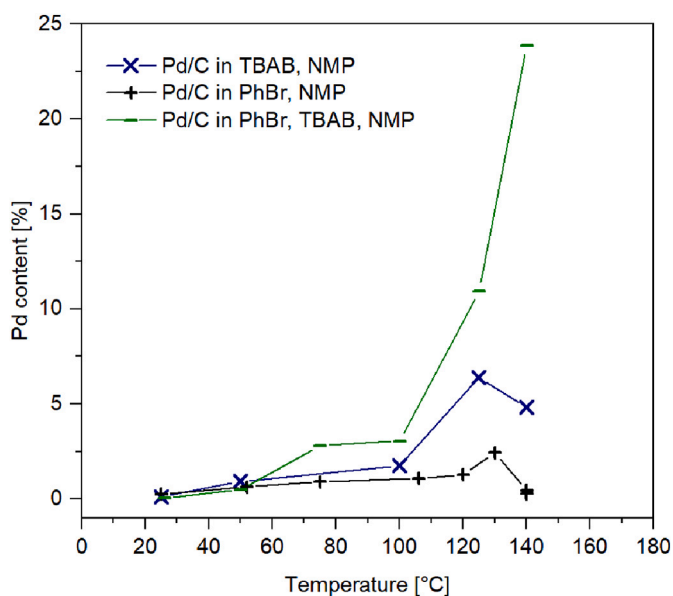


Fig. 3. Leaching of palladium from Pd/C (5 wt.-%) in NMP (250 mL) and bromobenzene (PhBr, 250 mmol) (+, black), 5 mmol TBAB (x, blue) or PhBr+TBAB (–, green). The curve shows the percentage of total Pd leached into solution as function of temperature and reaction time (temperature-programmed experiment); for detailed values of Pd in solution see SI, Table S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with significant increase of Pd concentration compared to exp. 1 and 2. In this case, the substrate, being able to undergo oxidative addition to the catalyst, is present as well as additional bromide ions, which are known to stabilize (ionic) palladium species in solution. [7] In the case of oxidative addition, the C–Br bond needs to be broken before oxidative addition can take place, this explains the higher set-off temperature, when bromide ions/TBAB are not present.

The results of analogous experiments with palladium supported on silica with a loading as low as 1 wt.-% Pd are shown in Fig. 4. Qualitative effects are identical, the percentage of Pd dissolved from the catalyst is substantially higher than with the 5% Pd/C catalyst (note the different scale of the y-axes in Fig. 3 and Fig. 4; for detailed values of Pd in solution see SI, Table S2). This is expected due to the substantial lower Pd loading (1 to 5 wt.-%). The latter experiments were continued as isothermal study, once the highest temperature had been achieved, i.e., we kept the temperature constant for some time (100 min). This is illustrated as a modified representation in Fig. S1 of the Supporting Information (SI) (time of the temperature-programmed experiments as x-axis). These experiments underline that Pd bromido complexes are not stable at higher temperatures. The steady increase of Pd concentration in solution with (isothermal) reaction time when PhBr is present only can be understood as due to progression of oxidative addition and lower total concentration of Pd in solution compared to experiments in Fig. 3. The leaching phenomena observed are not influenced by the support (SiO₂, C). This is not unexpected, because the dissolution starts from Pd particles and probably not from Pd-support interfaces.

Beyond the model simulations, a leaching experiment with styrene in NMP was carried out with the Pd/C catalyst too (Fig. S2 of the SI). Pd is leached also by styrene, starting slightly above room temperature, roughly linearly increasing up to 3% of total Pd at 130 °C. This is expected for the formation of a corresponding Pd-styrene- π -complex. At higher temperature, the Pd concentration decreases, which is expected due to reduction and agglomeration of palladium. The bromido and π -complex formation can also preferably start from Pd(II), bringing to mind the limitations of the simple model applied here, as Pd is often present in two different oxidation states (0, +II) in real catalysts. This

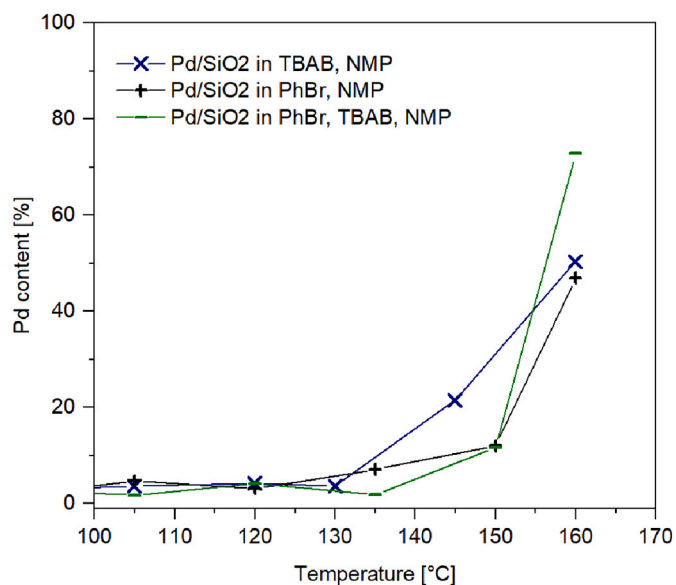


Fig. 4. Leaching of palladium from Pd/SiO₂ (1 wt.-%) in NMP (250 mL) and bromobenzene (PhBr, 250 mmol) (+, black), 5 mmol TBAB (x, blue) or PhBr+TBAB (–, green). The curve shows the percentage of total Pd leached into solution as function of temperature and reaction time (temperature-programmed experiment, cut-out of higher temperature part); for detailed values of Pd in solution see SI, Table S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aspect will be the subject of further investigations.

3. Conclusions

Palladium leaching from supported catalysts directly correlates with the rate of Heck coupling reactions. Model calculations of reaction free energies by DFT accompanied by closely targeted experiments rationalize that oxidative addition of phenyl bromide is decisive for decreasing the dissolution energy of palladium atoms. Additional bromide ions as predicted by calculations and shown in experiment clearly make the leaching process more exergonic. The effect of bromide ions is due to the high stability of the Pd(II) bromide complexes formed. Temperature-programmed leaching experiments show in addition that palladium leaching is also supported by bromide ions or styrene alone and that it is depleted with increasing temperature and time due to reductive precipitation.

Computational

All calculations were carried out with the linear combination of Gaussian-type orbitals fitting-functions density functional approach (LCGTO-FF-DF) to the Kohn-Sham problem as implemented in the code PARAGAUSS (Version 3.1.6). [29,30] All internal degrees of freedom were fully relaxed without any symmetry restriction; energies were calculated with the generalized gradient approximation (GGA) using the revised PBE [31] exchange–correlation functional. We used Gaussian-type basis sets of triple zeta quality following previous work. [32] We characterized all stationary points by a normal mode analysis ensuring that only structures representing local energy minima were considered. Free energies were evaluated by applying the harmonic oscillator approximation at 150 °C, 1 bar, starting from the normal modes. Long-range electrostatic solvation effects in the solvent DMF were accounted for using a polarizable-continuum approach, the COSMO (conductor-like screening model) method. [33]

Experimental

The catalytic reactions were carried out in three-necked round bottom flasks in air. In a standard leaching experiment, the flask is equipped with a magnetic stirring bar, an integrated thermometer, reflux condenser and septum. The qualitative and quantitative analyses of the reactants and products were performed by gas-liquid chromatography (GLC). The palladium content in solution was determined by either flame atomic absorption spectroscopy (FAAS), photospectrometrically or by ICP-OES. The catalysts are commercially available catalysts from Evonik (5 wt.-% Pd/activated carbon) and a self-made 1 wt.-% Pd/SiO₂ (Aerosil 200, Evonik) prepared by controlled deposition precipitation according to. [13] Average Pd particle sizes are 3 nm (Pd/C) and 2 nm (Pd/SiO₂). The standard procedure for the model Heck reaction is described in the literature. [13] More experimental details are given in SI.

CRediT authorship contribution statement

Katharina Wussow: Investigation, Writing – original draft, Methodology, Validation, Visualization. **Andrea Abram:** Investigation, Methodology, Validation, Visualization. **Klaus Köhler:** Conceptualization, Writing – original draft, Supervision, Resources, Writing – review & editing. **Chun-Ran Chang:** Formal analysis, Validation, Visualization. **Alexander Genest:** Supervision, Formal analysis, Software, Writing – review & editing. **Jun Li:** Supervision. **Notker Rösch:** Supervision, Formal analysis, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

C.R.C. gratefully acknowledges the hospitality at the Catalysis Research Center of TU Munich, where this work was carried out during his visit benefitting from the generous computing resources at Leibniz Rechenzentrum München. A.G. and N.R. thank Dr. Sven Krüger for valuable discussions and assistance. K.W. and A.A. acknowledge support of the TUM Graduate School. K.W., A.A., and K.K. thank Ulrike Ammari and the microanalytical laboratory at TUM for carrying out elemental analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2022.106441>.

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