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Supported homogeneous catalyst makes its own liquid phase

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ABSTRACT

A catalyst designed for homogeneous catalysis is shown to generate its own liquid phase if deposited onto a support. In this way, a macroscopically heterogeneous catalyst generates a microscopically homogeneous catalytic environment by self-organization.

2,2'-((3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)-bis(oxy))bis(4,4,5,5-tetraphenyl-1,3, 2-dioxaphospholane) modified rhodium complexes molecularly adsorbed onto porous silica powder show surprisingly high activity and regioselectivity in the gas-phase hydroformylation of propene to butanal, with no sign of deactivation. Operando IR investigations combined with density functional theory calculations confirm a side reaction: the aldol condensation of the butanal products. These heavier byproducts accumulate inside the pores of the catalytic material. IR and gas chromatography show a direct relation between formation of enones, products of the aldol condensation, performance, and stability of the catalytic system. This demonstrates that the aldol condensation products generated in situ act as a solvent providing an ideal environment to the impregnated homogeneous catalyst.

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1. Introduction

With an annual global production capacity of more than 10 million tons, hydroformylation is one of the largest applications of homogeneous catalysis in industry [1]. Alkenes are converted with syngas into aldehydes in the presence of a transition metal catalyst, with the linear isomer usually being the desired product.

These aldehydes are valuable intermediates for the synthesis of bulk chemicals such as alcohols, esters, amines, surfactants, and plasticizers [2]. Modern catalysts for shorter alkenes in the C2 to C8 range are predominantly based on rhodium modified by sterically demanding phosphine or phosphite ligands [3]. Reaction conditions are mild with 80–130 °C and 10–60 bar syngas pressure. Due to the high price of rhodium, efficient catalyst recycling is mandatory, and several immobilization strategies, for example

aqueous biphasic [4], micro-emulsions [5–7], ionic liquids [8,9], and supported liquids [10–15], have been investigated over the past decades in academia and industry. We have investigated the hydroformylation using molecularly

adsorbed ligand-modified rhodium complexes Rh-BzP on silica gel [16]. C2—C4 feeds were used as substrates and could be converted with high yield and minimal deactivation over 1000 h time on stream. Still, the catalyst performance was strongly dependent on the support structure and alkene feed. Immediate activity and selectivity were observed when using silica gel 100, a material with an average pore diameter of 11 nm. However, an induction period in which the catalyst gained activity within the first hours of experiment was observed using a silica material with an average pore size of 423 nm (Trisopor[®] 423), as shown in Fig. S1 (see the SI).

These observations combined with post-run analysis of the Rh—SiO₂ catalyst suggest the following hypothesis: The smaller pores of silica 100 enhance the capillary condensation of the aldehydes formed. This quickly facilitates the consecutive aldol condensation reaction that provides the ideal solvent environment for the rhodium catalyst (Scheme 1a and Fig. 1). Indeed, the enone





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resulting from aldol condensation, also called heavies, is a excellent solvent for PPh₃-modified (Ph = phenyl) rhodium in industrial hydroformylation, namely the UCC liquid recycle process [17–20]. These enone formation processes, which can be catalyzed by the acidic silica support, are much slower in the larger pores. However, evidences for such a catalyst generating itself an ideal environment require a direct investigation of the enone formation. Here, we investigated the behavior of a Rh—SiO₂ catalyst (Scheme 1b) in the hydroformylation of propene with diffuse reflectance IR spectroscopy (DRIFTS) [21].

2. Materials and methods

2.1. Chemicals

Rh(CO)₂(acac), methanol, and dichloromethane (HPLC grade) were purchased from Sigma Aldrich and used without further purification. The BzP ligand 2,2'-((3,3'-di-*tert*-butyl-5,5'-dimethoxy-biphenyl-2,2'-diyl)bis(oxy))bis(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane) was supplied by Evonik Industries AG, Marl, Germany. Silica gel 100 (63–200 μ m) was purchased from Merck, and Trisopor[®] 423 (100–200 μ m) from VitroBio GmbH. The SiO₂ materials were thermally pre-treated at 600 °C for 18 h before usage in catalyst preparation. Propene (99.5%), carbon monoxide (99.97%), and hydrogen (99.999%) were purchased from Linde AG.

2.2. Catalyst preparation

All syntheses were carried out using standard Schlenk technique under Argon (99.999%). Rh(CO)₂(acac) was dissolved in dichloromethane and stirred for 5 min. The ligand was added in fivefold molar excess (ligand/Rh = 5), dissolved in dichloromethane, respectively, and the resulting solution was stirred for 5 min. After addition of appropriate amount of calcined silica 100 or Trisopor[®] 423, the suspension was stirred for another 10 min. The organic solvent was removed by using a rotatory evaporator, and the dry powder was further dried under vacuum (1 × 10⁻⁴ bar) over night.

2.3. Kinetic experiments

The experiments were conducted in a tubular reactor setup previously described [15,22]. The catalyst was placed inside the reactor, and a pre-mixed gas feed was passed over the bed. Online analysis was carried out using an Agilent 7890A GC with a 1-mL sampling loop, equipped with a GS-GasPro capillary column (Agilent Technologies, length 30 m, inner diameter 0.32 mm) and a flame ionization detector (FID).

2.4. Operando experiments

The catalyst characterization was performed in a Bruker Vertex 80v IR spectrometer equipped with a homemade sample compartment cover. This cover is equipped with all necessary feedthroughs to lead the gas in and out of the reactor, and control and measure the temperature while keeping the optical path completely evacuated during the measurements. DRIFTS was performed in a praying mantis using a high-temperature reaction chamber (HVC-DRP-4) from Harrick. The reactor was modified to include a type K thermocouple measuring the temperature directly in the powder. Mass flows and pressures were regulated using Bronkhorst mass flow and pressure controllers. Prior to the start of the reaction, the catalyst powder was heated under an Ar flow (5 mL_s min⁻¹, 2 bar) at 80 °C for 3 h to desorb water and solvent residues. The experimental protocol is further detailed in the main text. IR spectra were recorded with a spectral resolution of 2 cm⁻¹, 151 scans, and a scanning speed of 40 kHz yielding an acquisition time of 60 s per spectrum. Online gas chromatography was performed on an identical GC setup as in the kinetic experiments. The gas stream was injected every 10 min into the column, which was kept at 200 °C (see Fig. S1 for an excerpt of the chromatogram). All gases were used without further purification (Ar, Linde, >99.9999%; propene, Linde, >99.8%; H₂, Linde, >99.999%; CO, Linde, >99.997%; He, Linde, >99.996%; synthetic air, Linde, 80% N₂ 20% O₂, hydrocarbon free; N₂, Linde, >99.999%).

2.5. Computational details

Density functional theory (DFT) [23] calculations were carried out using the TURBOMOLE program package [24,25]. The



Scheme 1. (a) Reaction sequence of hydroformylation followed by aldol condensation and (b) equilibrium for diphosphite-modified rhodium complexes and structure of 2,2'- ((3,3'-di-*tert*-butyl-5,5'-dimethoxy-biphenyl-2,2'-diyl)bis(0xy))bis(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane) (abbrev. BzP).



Fig. 1. Illustration of the process of pore filling with aldehyde and aldol products during the catalytic hydroformylation reaction using ligand-modified Rh complexes in porous silica supports.

gradient-corrected exchange-correlation functional due to Becke [26] and Perdew [27] was used in combination with the resolution-of-the identity technique (RI). A triple-zeta-valence-polarized (TZVP) basis set [28] together with the corresponding auxiliary basis set [29] obtained from the TURBOMOLE basis set library was used. All calculated molecules have been fully optimized in the gas phase without any symmetry or other constrains. No imaginary frequencies were obtained in the frequency calculations. The energy difference between the *Z*- and *E*-enone was found to be 2.7 kcal mol⁻¹ in favor of the *E*-enone. Visualization of the calculated frequencies was performed using Vibeplot [30].

3. Results and discussion

3.1. Comparison between tubular reactor and DRIFTS reaction cell

The reaction chamber for the DRIFTS cell can be operated at a maximum pressure of 2 bar while the usual hydroformylation conditions are 10 bar. In order to compare the performance of the Rh-SiO₂ catalyst, low-pressure experiments were conducted in the tubular reactor under close to identical conditions (with a residence time of 4.1 s in the DRIFTS reactor and 6 s in the tubular reactor, details on the reactor designs are provided in SI). Propene was used as substrate because it was more accurate to dose via mass flow controllers compared to alkenes with a higher carbon number. It was expected that the condensation of the produced butanal and therefore the formation of the enone film occur on a longer timescale under the conditions applied, making it easier to study the transient behavior in both reactor types. Online GC analysis provided conversion and selectivity over time as depicted in Fig. 2.

Despite the different designs of the reactors, the results were very similar over the tested 160 h on stream. In both experiments, propene conversion started from 0% and increased rapidly over the first 6 h. Conversion reached a steady state after approx. 30 h time on stream for which 1.6% was determined in the operando reactor and 2.1% in the tubular one. The selectivity to linear butanal already reached a steady state after 12 h with values of 98% in the operando and 97% in the tubular reactor. These values are slightly lower than in previous experiments using the same Rh-BzP catalyst species, presumably due to the lower pressure in the present case. Three stages of operation are identified from the gas chromatogram shown in Fig. 2: In the first 6 h, the catalyst showed an activation period (stage 1), where both conversion and *n/iso*-selectivity changed significantly. In the second period,



Fig. 2. Conversion (top) and selectivity (bottom) measured online behind the tubular reactor (open symbols) and operando in the IR reactor (full symbols). The selectivity toward 2-ethylhex-2-enal was measured online within the first 110 h in the tubular reactor experiment. Reaction conditions: $m_{cat} = 700 \text{ mg}$ (for operando IR reactor: 60 mg), $m_{Rh} = 0.2 \text{ wt.\%}$, L/Rh = 5, $T = 80 \,^{\circ}\text{C}$, p = 2 bar, $p_{propene} = 0.4 \text{ bar}$, $p_{H2} = p_{CO} = 0.8 \text{ bar}$, residence time = 6 s (for operando IR reactor: 4.1 s).

between 6 and 30 h, these changes became less pronounced and the selectivity reached its steady state value while the activity was still slowly increasing (stage 2). Finally, the steady state where both activity and *n*/*iso*-selectivity remained unchanged over time on stream was reached after 30 h (stage 3). The selectivity toward the aldol product was also low in the beginning and increased rapidly during the first 6 h on stream in the tubular reactor. After reaching a maximum selectivity of about 3% after about 18 h, the amount of enone in the gas phase decreased over the whole experiment. In addition, the reaction gas flow was cut off after 115 h in the tubular reactor experiment, and the catalyst was stored under helium inert gas overnight. Upon restart of the reaction, the system almost instantaneously showed the very same catalytic performance as before. Here, no prolonged activation period was observed, indicating that the catalyst material was already activated when the hydroformylation reaction continued.

3.2. Operando DRIFTS measurements

Operando DRIFTS complements this reactivity study and enables a better understanding of the nature of the three stages identified. Fig. 3 displays the first and last 6 h of the total experiment over 218 h. The difference spectra display the changes with respect to the initial state of the sample.

Introduction of the reactants at 10 min was identified by the rapid appearance of bands around 2100 cm⁻¹ (CO), and additional

ones at 1000, 1450, 1600, and 3000 cm^{-1} that are all attributed to the presence of propene. Note that H₂ cannot be observed with IR but was nevertheless introduced with the other gases. The intensity of the gas-phase signals stabilized after 60 min. IR bands then developed at 1723, 2066, 2750–3000, and 3200–3600 cm⁻¹. The



Fig. 3. Time series during the DRIFTS operando experiment shown as a grayscale surface plot. Experiments were conducted under a constant total pressure of 2 bar, a mixture of H_2 :CO:propene (ratio 2:2:1) flowing at 2.5 mL_s min⁻¹ total flow, at 80 °C. After 213 h, the reactor was cooled down to 30 °C under the same flow rate. At 216 h, the reactor was purged with Ar (10 mL_s min⁻¹).



Fig. 4. Time-resolved operando DRIFTS spectra of the CO region acquired after selected times between 30 min and 96 h. The gas-phase signals of CO and propene were subtracted according to the procedure described in supporting information. (a) $1950-2200 \text{ cm}^{-1}$ region; (b) $1600-1800 \text{ cm}^{-1}$ region; (c) amplitudes from a; and (d) amplitudes from b. IR spectra were recorded for approximately 16 h a day for 5 days. The reaction continues in the blank regions in (c) and (d), but IR was not measured due to practical limitations.

large contribution at 3200–3600 cm⁻¹ is attributed mostly to condensation of water on the liquid-nitrogen-cooled MCT detector. The strong increase in the signal after 213 h, when the reactor was cooled to 30 °C, suggests condensation of water in the pores of the catalyst that can come from aldol condensation that liberates water (Scheme 1a) and possibly also from wet propene or CO feeds. After 216 h, the reactor was purged with $10 \text{ mL}_{s} \text{ min}^{-1}$ Ar, as can be seen from the disappearance of the gas-phase and water signals. Interestingly, the bands previously observed at 1723, 2066, and $2750-3000 \text{ cm}^{-1}$ and another band at 2144 cm⁻¹ remain visible after removal of all reactants. The band at 2066 cm⁻¹ is attributed to the most active absorption resulting from the formation of the monomeric catalyst complexes [31], the band at 1723 cm⁻¹ to C=O stretching vibrations in the products, and the bands at 2750–3000 cm⁻¹ to C–H stretching in the reaction products.

From this overview, it is clear that operando DRIFTS experiments have the potential to give information on the activation of the catalyst, the reactants, and the products in real time and under gas-phase hydroformylation.

Fig. 4 shows selected spectra in the CO region, (a) from 2200 to 1950 cm^{-1} and (b) from 1800 to 1600 cm⁻¹. In Fig. 4a, the band at 2114 cm^{-1} and its shoulder expanding to 2050 cm^{-1} readily

0

i DFT- E-enone

absorption 100 km/mol

ii DFT- Z-enone

appeared upon introduction of CO in the reactor. The band reached a maximum after about 6 h and then slightly decreased with time (see Fig. 4c). The band already identified at 2066 cm^{-1} increased together with three other bands at 2040, 2012, and 1986 cm^{-1} . The evolution of these four bands over time was parallel throughout. Their intensity increased during the first 20 h and reached near saturation at above 60 h. These bands characterize the complex isomers formed upon activation of the catalyst precursor by ligand and syngas, shown in Scheme 1b [31].

The band at 2114 cm⁻¹ and its shoulder are consistent with isolated gem-dicarbonyl Rh(CO)₂ [32-34]. These Rh(CO)₂ species were formed as soon as CO was added and indicate the presence of highly dispersed Rh that is probably the result of a small amount of catalyst decomposed during the pre-treatment of the catalyst (see experimental section). Despite the presence of these isolated Rh atoms, no sign of sintering or formation of particles was observed, which would display the characteristic linear-bound CO at 2080 cm⁻¹ [34,35]. Fig. 4b shows the absorption band already identified at 1723 cm⁻¹ and a less intense band at 1670 cm⁻¹. It appeared that the band at 1723 cm⁻¹ intensified first, approaching steady state after 6 h. The band at 1670 $\rm cm^{-1}$ was first observed after 6 h and kept growing over the whole experiment. This could indicate that this later band stemmed from a by-product

absorption

20 km/mol



calculated frequencies. A 5× magnification factor was applied to the fingerprint region (wavenumbers below 1500 cm⁻¹). Simplified visualization of the individual normal modes of the products; (iv) *E*-enone, (v) *Z*-enone and (vi) *n*-butanal (raw output can be found in the SI). The thickness of the lines representing the individual modes is proportional to the stretching amplitude of the respective mode. The phase of the displacement is reflected by different colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the reaction. At this point, however, unambiguous assignment of the absorption features of the products is not possible.

For this reason, the spectra for the *E*-enone, *Z*-enone, and *n*-butanal were calculated using density functional theory (DFT). A zoom on the 1600–1800 cm⁻¹ region is shown for comparison with Fig. 4b. The E-enone and the Z-enone both feature an intense absorption at 1692 or 1675 cm⁻¹ (resp.) and a less intense absorption at 1633 or 1626 cm⁻¹ (resp.). This pattern is qualitatively comparable to the experimental spectra acquired operando and to the reference measurements (cf. Figs. 4b and S4). The frequencies obtained are also within the accuracy expected from harmonic calculations of free molecules compared to the real system. Fig. 5iv-vi shows the visualization of the corresponding vibrational modes in terms of changes of internal coordinates [30]. It appears that the vibrations at higher frequencies [$v_{55}(E-and Z-enone)$ and $v_{31}(n-butanal)$ are due to stretching of the CHO groups and the vibrations at lower frequency $[v_{54}(E-\text{ and } Z-\text{enone})]$ to stretching vibrations of the C=C enone double bond.

With the help of the DFT calculations, the band observed experimentally at 1670 cm⁻¹ can be attributed unambiguously to the enones, whereas the band observed at 1723 cm⁻¹ contains contributions from both n-butanal and the aldol condensation products. Comparison of the evolution of these signals during the experiment (Fig. 4d) with the GC experiments (Fig. 2) displays a remarkable agreement. Furthermore, the highest aldol condensation rate coincides with the high butanal production rate over the first 6 h. After stabilization of the butanal signal, the aldol condensation rate decreases steadily without ever reaching a steady state. We can therefore conclude that butanals are produced first up to an equilibrium concentration in the pores, followed by formation of enone by-products at a lower rate. These findings validate the pore-filling model illustrated in Fig. 2, in which aldehyde and aldol products condense inside the porous network of commonly used silica materials during the course of the reaction.

4. Conclusions

The combination of a 218-h-long operando DRIFTS experiment and density functional calculations of the resulting IR spectra gave clear evidence that the BzP-modified Rh complex generates a liquid enone phase in the pores of the silica substrate on which it is adsorbed. The environment generated by the catalyst was shown to provide favorable reaction conditions leading to good activity and high robustness of the hydroformylation catalyst. The experiment was furthermore reproduced under the same conditions in a tubular fixed-bed reactor, and comparison of the experiments in both types of reactor leads to a very good agreement. The experiments showed that operando IR spectroscopy is a perfectly suited method to study a homogeneous catalytic reaction as it allowed to simultaneously identify the reactants, the formation of the active catalyst (*ee* and *ea* monomers), the formation of the reaction products (aldehydes) and of the by-products (enones).

Three stages were identified in the reaction that can be summarized as follows.

Stage 1. The activation of the catalyst, that is, formation of the (ee) and (ea) monomers took place during the first 6 h of the experiment, which was identified as stage 1 in the kinetic experiments using GC analysis. In the same period, mainly *n*-butanal formed inside the pores of the catalyst, thereby dissolving more and more of the molecularly adsorbed rhodium complex. Accordingly, the butanal formation rate increased with increasing quantity of active catalyst. Furthermore, GC measurements show that the activity and the *n*/*iso*-selectivity were lower in this first period than at steady state.

Stage 2. Once the concentration of product in the pores reached equilibrium and most of the catalyst had been activated and dissolved, the enone by-product started forming, providing an even better solvent for the catalyst. There, the activity increased while the regioselectivity remained constant.

Stage 3. Aldol condensation occurred over the whole experiment, but at a rather low rate under our experimental conditions. This formation of enone coincided with the stabilization of the catalytic properties observed in the kinetic experiments. Despite the increasing amount of enone, we could not detect a decrease of the butanal concentration in the pores of the catalyst or in the gas phase as could be expected from filled pores.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.10.019.

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