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# Ligand-Modified Rhodium Catalysts on Porous Silica in the Continuous Gas-Phase Hydroformylation of Short-Chain Alkenes—Catalytic Reaction in Liquid-Supported Aldol Products

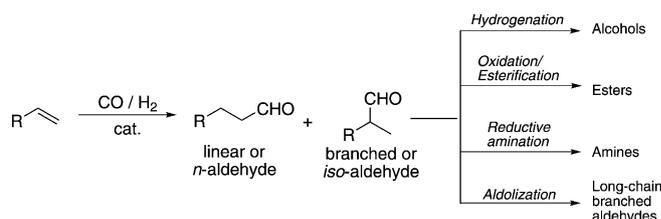
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Ligand-modified Rh complexes were physically adsorbed on the surface of porous silica. The resulting materials were subjected to the continuous gas-phase hydroformylation of C<sub>2</sub> and C<sub>4</sub> alkenes. The ligands used for catalyst modification were bidentate phosphorus ligands known from the literature, namely, sulfoxantphos (**1**) and a benzopinacol-based bulky diphosphite **2**. The tested catalyst materials were active and, in particular, selective as in comparable homogeneous liquid-phase experiments. Long-term stability experiments over 1000 h on stream showed minor deactivation. A significant increase in the cata-

lyst mass after the reaction was detected by weighing and thermogravimetric analysis. By using headspace-GC-MS, the mass increase could be attributed to high-boiling compounds, which are formed in situ during the catalytic reaction itself and accumulate inside the pores of the support. Evidence is given that the initially physisorbed catalyst complexes dissolve in the high-boiling aldol side-products, which are suitable solvents for the active catalyst species and provide a liquid-phase environment held by capillary forces on the support.

## Introduction

Hydroformylation is one of the most common homogeneously catalyzed processes worldwide. With an annual production of oxo products beyond 10 million tons, this reaction is of high technical relevance in the chemical industry.<sup>[1]</sup> In hydroformylation, alkenes react with synthesis gas (syngas), a mixture of H<sub>2</sub> and CO, to form aldehydes, which are valuable intermediates for the synthesis of bulk chemicals such as alcohols, esters, and amines (Scheme 1).<sup>[2]</sup> Long-chain alcohols with a doubled carbon number are accessible through consecutive aldolization reactions. The majority of today's hydroformylation processes utilize homogeneously dissolved, Rh-based organometallic catalytic complexes, which operate under relatively mild reaction conditions in contrast to cobalt systems, that is, temperatures in the range of 85–130 °C and pressures in the range of 15–



**Scheme 1.** Catalytic hydroformylation of terminal alkenes to yield aldehydes (*n* and *iso*) and possible consecutive reaction pathways to bulk chemicals.

60 bar.<sup>[3]</sup> In the well-known Ruhrchemie-Rhône/Poulenc process, very efficient catalyst recycling and product separation has been established by the use of an aqueous/organic biphasic reaction system.<sup>[4]</sup> Since the successful start of this process almost 30 years ago, numerous immobilization techniques for homogeneous catalysts have been developed and reported, and many of these concepts have been exemplified for hydroformylation catalysis.<sup>[5]</sup> Amongst these, the heterogenization of catalyst complexes by immobilization on porous support materials has been extensively studied. Such heterogenization can be achieved by, for example, covalently anchoring the Rh complex onto the support by spacer ligands.<sup>[6]</sup> Furthermore, the metal complex can be dissolved in an appropriate liquid, and the resulting solution dispersed onto the surface of a porous solid support. Depending on the liquid, so-called supported liquid-phase (SLP),<sup>[7]</sup> supported aqueous-phase (SAP)<sup>[8]</sup> or supported ionic-liquid-phase (SILP)<sup>[9]</sup> catalysts have been obtained. In particular, the SILP concept is ideally suited for continuous gas-phase processes because of the extremely low vapor pressure of the ionic liquid solvent. Long-term stability of more

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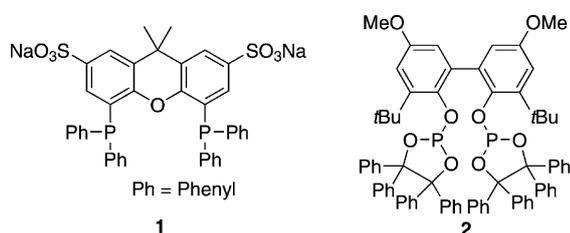
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than 800 h on stream has been reported for  $C_4$  hydroformylation on application of these SILP systems.<sup>[10]</sup> Bulky bidentate diphosphine and diphosphite ligands have been used to ensure high selectivity to the desired linear aldehyde.<sup>[11,12]</sup>

In one of the first reports on the SILP-catalyzed hydroformylation of propylene, some of us reported a small decrease of catalyst activity over time because of the formation of high-boiling side-products, however, the initial activity was easily restored by a vacuum procedure.<sup>[13]</sup> To investigate the influence of possible aldol condensation products on the hydroformylation reaction in the gas phase, we prepared catalyst materials according to a similar procedure as for the established synthesis of SILP catalysts (incipient-wetness impregnation)<sup>[9]</sup> but without adding ionic liquid. The as-prepared, purely physisorbed Rh complexes on  $SiO_2$  (modified with sulfoxantphos (1) and a benzopinacol-based bulky diphosphite 2 ligand, respectively; Figure 1) were tested in the continuous gas-phase hy-



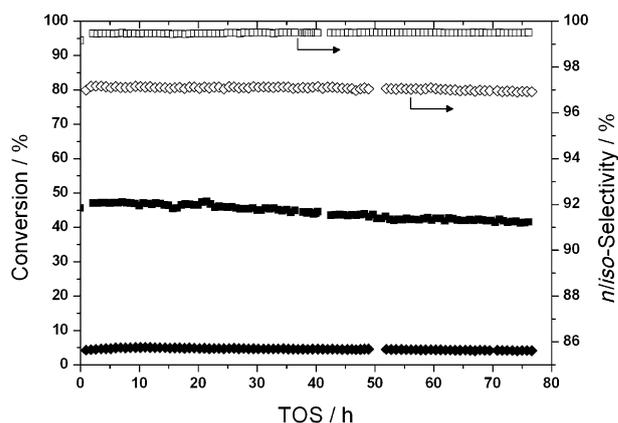
**Figure 1.** Bidentate ligands used in (SILP) hydroformylation catalysis to achieve high regioselectivities: sulfoxantphos (1) and benzopinacol-based ligand (2).

droformylation of short-chain alkenes. In this contribution, we demonstrate that, under the reaction conditions applied, a liquid phase that consists predominantly of aldol condensation products forms in situ inside the pores of the supporting silica and acts as suitable solvent for the active hydroformylation catalyst. With the catalytically active species dissolved in these high-boiling compounds, the catalyst materials showed the same *n/iso* selectivities as those typically found for classical homogeneous systems. Analysis of the spent catalysts after reaction indicates that the filling of the pores with high-boiling compounds is a function of the reaction conditions, the degree of conversion and the porosity of the silica support. The long-term stability of the Rh-2/ $SiO_2$  system was tested under the optimized conditions for a technically relevant  $C_4$  feedstock.

## Results and Discussion

### Catalytic investigations

After deposition of the Rh-1 catalyst complex on porous silica 100 (calcined at 600 °C for 12 h prior to catalyst preparation) by incipient-wetness impregnation, the resulting material was tested in the continuous gas-phase hydroformylation of 1-butene. Surprisingly, this essentially solvent-free catalyst complex showed considerable stability over 70 h on stream in this purely physisorbed state with only minor deactivation as de-

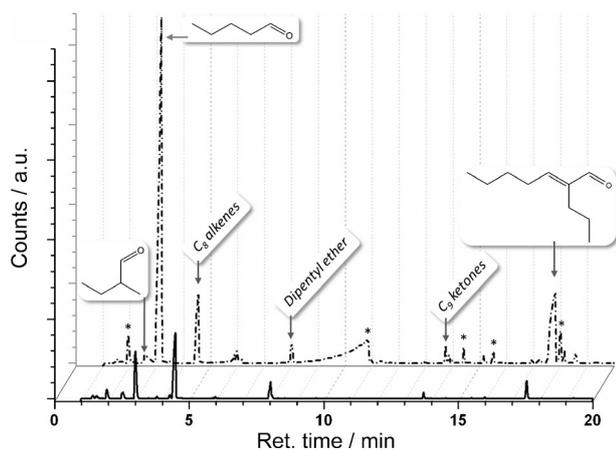


**Figure 2.** Conversion and selectivity over time of the continuous gas-phase hydroformylation of 1-butene using Rh-1 (◆, ◇) and Rh-2 (■, □) catalyst complexes on silica 100; parameters:  $m_{cat} = 2.3$  g,  $m_{rh} = 0.2$  wt%,  $L/Rh = 5$ ,  $T = 100$  °C,  $p_{total} = 10$  bar,  $p_{1-butene} = 1.8$  bar,  $p_{H_2} = p_{CO} = 4.1$  bar, residence time = 20 s.

icted in Figure 2. Furthermore, the catalyst selectivity towards the linear aldehyde product, *n*-pentanal, was 97%. This value is in good agreement with literature data for Rh-1 catalysts in homogeneous liquid-phase and SILP systems.<sup>[9,14]</sup> The share of hydrogenation side-products in the product mixture was below 5%. On using the Rh-2 catalyst complex in the same physisorbed state on silica 100, a comparable high stability was observed even though 2 is a diphosphite ligand and thus prone to decomposition by hydrolysis. A maximum degree of conversion of 47.3% related to 1-butene was detected for the Rh-2/silica100 material compared to 5.1% in the case of Rh-1/silica100. The higher catalytic activity of the Rh-2-based system results from the chemical nature of 2. The diphosphite ligand 2 is known to provide a better  $\pi$ -acceptor ability that strengthens the Rh-to-ligand bonding, which facilitates CO dissociation and alkene association within the catalytic cycle.<sup>[12]</sup> The hydrogenation activity of the Rh-2/silica100 system was around 7%, and the regioselectivity reached a value of 99.5%. Again, this very high selectivity for the formation of the *n*-pentanal product is in good agreement with previous experiments that used Rh-2 in a bulk liquid environment.<sup>[15]</sup> A closer look at the degree of conversion over time on stream (TOS) reveals that slight deactivation occurred for both catalyst systems. In the case of Rh-1/silica100, the conversion dropped from 5.1 to 4.3% over 70 h on stream, which corresponds to a decrease in turnover frequency (TOF) from 90.5 to 75.2  $h^{-1}$ . For the Rh-2/silica100 system, the degree of conversion decreased from 47.3 to 41.5% (which corresponds to a drop in TOF from 750.7 to 658.6  $h^{-1}$ ) over the same operation time. Nonetheless, the observed catalyst stabilities are surprisingly high if we take into account that the applied Rh complexes were initially supported on dry silica (traces of solvent from the incipient-wetness impregnation are not excluded). No liquid phase has been offered to explicitly provide a solvent environment for the Rh complexes that are usually applied and known to work best as homogeneous catalysts.

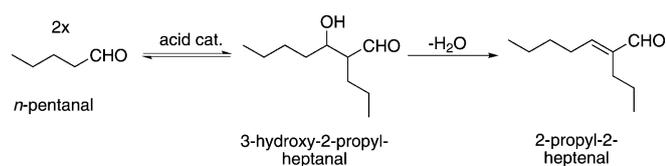
To elucidate these remarkable catalyst stabilities, we had a closer look at the full product spectrum during continuous

catalytic operation. In addition to the  $C_5$  aldehyde products measured by online GC, traces of aldol compounds were detected for both the Rh-1 and Rh-2 catalyst systems. We weighed the catalyst materials after 70 h on stream, which revealed an increase in mass of 5.2 and 29.1% for the two catalysts, respectively, in comparison to the material initially put into the reactor. Combined headspace-GC-MS analysis of the spent catalysts showed the presence of considerable amounts of aldehyde and aldol products alongside with other high-boiling compounds, which clearly remained inside the porous materials after recovery from the reactor. The main signals can be attributed to linear pentanal and the  $C_{10}$  aldol condensation product, 2-propyl-2-heptenal (Figure 3). The latter is formed by



**Figure 3.** Headspace-GC-MS analysis of used Rh-1 (—) and Rh-2 (---) catalyst materials. Both catalysts showed stable catalytic performance over 70 h on stream in the continuous hydroformylation of 1-butene. The main products are labeled with chemical structures; side signals are labeled with names as different isomers may be present.

the consecutive reaction of the linear aldehyde product probably catalyzed by the surface acidity of the silica support (Scheme 2). The intermediate aldol addition product, 3-hydroxy-2-propylheptanal, was not detected. Further signals were attributed to *iso*-pentanal,  $C_8$  alkenes, ketones, and dipentyl ether, which originate from other consecutive reaction pathways of the produced linear pentanal. The other signals visible in the spectrum in Figure 3 stem from support or ligand decomposition compounds (indicated by \*) as determined by reference measurements of the freshly prepared catalyst materials. Traces of organic solvents used in the catalyst preparation were also detected.



**Scheme 2.** Consecutive reaction of linear pentanal to form a  $C_{10}$  aldol condensation product, 2-propylhept-2-enal.

If we compare the signal intensities in the headspace-GC-MS spectra, it is evident that under the conditions applied during continuous hydroformylation ( $p_{\text{total}} = 10$  bar,  $p_{1\text{-butene}} = 1.8$  bar,  $T = 100$  °C) the produced pentanals undergo consecutive reactions to a considerable extent to form predominantly the  $C_{10}$  aldol condensation product. The relatively low vapor pressure of these aldols (and the other high-boiling compounds) clearly leads to an in situ formation of a liquid aldol phase inside the smallest pores of the porous silica 100 support.

Notably, the catalyst materials remained free-flowing powders even after prolonged time on stream, which indicates that a vapor-liquid equilibrium of high-boiling compounds is reached under steady-state reaction conditions. This assumption will be discussed in detail below. As the tested catalytic materials showed high regioselectivities similar to the behavior known from classical homogeneous systems, it is proposed that the high-boiling products dissolve the initially physisorbed Rh-1 and Rh-2 catalyst complexes, respectively, to provide a liquid-phase environment for the catalytically active species inside the pores of the support. According to the literature, purely heterogeneous catalysts suffer from low hydroformylation activity and rather high hydrogenation activity if applied in gas-phase contact.<sup>[16]</sup> Without the presence of a liquid reaction phase, in which the organometallic catalyst complex is dissolved, poor regioselectivity is often found as well. Early publications report active and selective hydroformylation catalysts if Rh-TPP (triphenylphosphine) complexes are used on silica supports.<sup>[7]</sup> In these cases, TPP is a liquid under the reaction conditions applied and serves as both the ligand and the solvent of the Rh catalyst complexes. As the melting points of **1** and **2** are higher than the reaction temperature, this contribution can be excluded in the present study. According to the literature, selective and stable hydroformylation catalysts can be obtained from  $\text{Rh}^0/\text{SiO}_2$  in the presence of syngas by in situ formation of  $\text{Rh}(\text{CO})_2$  species from Rh nanoparticles followed by ligation of a phosphine ligand, such as TPP.<sup>[17]</sup> Even xantphos-modified  $\text{Rh}^0/\text{SiO}_2$  systems have been published recently that were found to behave similarly to comparable liquid-phase or SILP catalysts with respect to kinetic and spectroscopic characterization.<sup>[18]</sup> These catalytic materials, however, were investigated under reaction conditions that should strongly minimize aldol formation and condensation, that is,  $p_{\text{total}} = 2$  bar and alkene conversion  $< 1\%$ . The fact that ligand-modified Rh complexes are active and highly regioselective in liquid aldols is not surprising as this principle is applied on a million-ton-scale in the industrial low pressure oxo (LPO) process, developed by the Union Carbide Corporation (UCC).<sup>[19]</sup> However, to the best of our knowledge, the concept of the immobilization of ligand-modified Rh complexes by the in situ formation of high-boiling compounds in the confined space of porous support materials for gas-phase application has not been reported elsewhere.

By using the Kelvin equation<sup>[20]</sup> [Eq. (1)], which describes the change in vapor pressure of a pure compound at curved liquid-vapor interfaces, such as, for example, in the capillaries of a porous support, it is possible to estimate whether the con-

condensation of pentanals and/or C<sub>10</sub> aldols occurs under the conditions of a specific catalytic experiment inside the pores of silica 100. Using highly porous materials as the catalyst support, the vapor pressure of the hydroformylation products is reduced significantly, which promotes the condensation of low-volatility compounds that would be gaseous without the confinement. Therefore, the following estimations are relevant for the present study.

$$p = p_s \cdot \exp\left(-\frac{2 \cdot \sigma \cdot M}{RT \cdot \delta_l} \cdot \frac{1}{r_{\text{pore}}}\right) \quad (1)$$

The parameters used in Equation (1) are saturation vapor pressure  $p_s$ , surface tension  $\sigma$ , molar mass  $M$ , universal gas constant  $R$ , temperature  $T$ , liquid density  $\delta_l$ , and pore radius  $r_{\text{pore}}$ . Even though the Kelvin equation is only valid for pure compounds and a complex gas mixture is present in the case of the hydroformylation catalysis under investigation, the equation was applied here for a first estimation of possible pore condensation phenomena. The surface tension  $\sigma$  was calculated from an empirical formula according to Brock and Bird based on critical parameters ( $p_c$ ,  $T_c$ , and the normal boiling point temperature  $T_{\text{NBP}}$ ) [Eqs. (2) and (3)].<sup>[21]</sup>

$$\sigma = (p_c)^{2/3} \cdot (T_c)^{1/3} \cdot Q \left(1 - \frac{T}{T_c}\right)^{11/9} \quad (2)$$

with

$$Q = 0.1196 \left[1 + \frac{T_{\text{NBP}} \cdot \ln\left(\frac{p_c}{1.01325}\right)}{1 - \frac{T_{\text{NBP}}}{T_c}}\right] - 0.279 \quad (3)$$

All other necessary physicochemical data are compiled in Table 1 (values stem from the FLUIDAT database provided by Bronkhorst High-Tech B.V., the Netherlands). From Equation (1), the vapor pressure of *n*-pentanal was calculated as 0.74 bar

Table 1. Characteristics of <i>n</i> -pentanal and <i>n</i> -decanol at $T=100^\circ\text{C}$ and $p=10$ bar. Values labeled with * were taken from the FLUIDAT database, Bronkhorst High-Tech B.V., the Netherlands.							
Compound	$p_s$ [bar]	$p_c$ [bar]	$T_c$ [K]	$T_{\text{NBP}}$ [K]	$\sigma$ [m Nm <sup>-1</sup> ]	$\delta_l$ [kg m <sup>-3</sup> ]	$M$ [g mol <sup>-1</sup> ]
<i>n</i> -Pentanal	0.93*	35.5*	554.0*	375.8*	16.65	685.7*	86.1
<i>n</i> -Decanol	0.013*	22.3*	700.0*	513.1*	23.72	790.7*	158.3

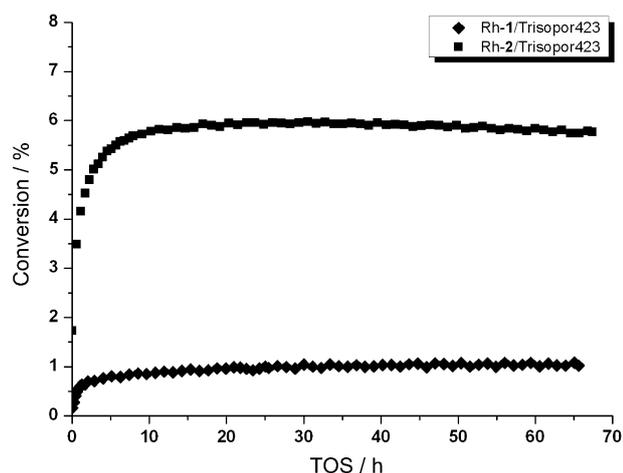
with respect to the reaction conditions applied, that is,  $T=100^\circ\text{C}$ ,  $p=10$  bar, and a mean pore radius of silica 100 of 6 nm as determined from N<sub>2</sub> adsorption measurements. Regarding the micropores only (mean pore radius of 1 nm), the value further reduces to 0.24 bar. For the observed degree of conversion, an *n*-pentanal partial pressure of 0.10 and 0.52 bar in the feed gas was determined for the Rh-1 and Rh-2 catalyst systems. These partial pressures are below the estimated condensation pressure of 0.74 bar, which takes into account the total

pore fraction of the support. The condensation of produced pentanals might occur in the micropores for Rh-2 because of the pore size distribution of silica 100 as here the observed *n*-pentanal partial pressure is above the value of 0.24 bar. In the case of Rh-1/silica100, pentanal condensation should not be relevant because of the significantly lower degree of conversion. This situation changes on considering the aldol products. As a result of the lack of physical data for 2-propyl-2-heptenal, *n*-decanol was chosen as a comparable C<sub>10</sub> compound for a first approximation. Under the reaction conditions, the saturation partial pressure of *n*-decanol is already very low ( $p_s=13 \times 10^{-3}$  bar). If we take the confined space in the pores of silica 100 into account, the condensation vapor pressure is further reduced to  $0.6 \times 10^{-3}$  bar. If we assume that the value for C<sub>10</sub> aldol is of the same order of magnitude, it is not surprising that a considerable amount of aldol and other high-boiling products are found in the pores of the spent catalyst materials as shown in Figure 3. The detected amount of pentanals might be a result of capillary condensation or dissolved matter in the higher boiling C<sub>10</sub> aldols.

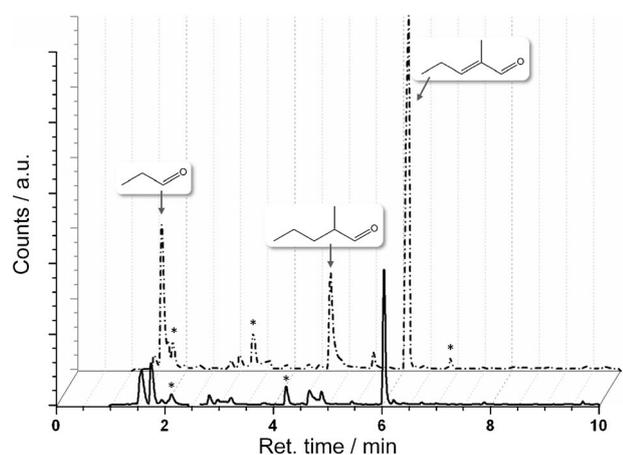
To evaluate the conditions under which the formation and accumulation of low-volatility organic compounds inside the porous network of the catalytic materials occur, both the supporting silica and alkene substrate were varied. The micro-/mesoporous silica 100 was replaced by a macroporous SiO<sub>2</sub> material, namely, Trisopor 423, which was expected to suppress the extent of pore condensation by providing pores with an average diameter of 423 nm instead of 11 nm as in the case of silica 100. After immobilization of the Rh-1 and Rh-2 catalyst complexes on this macroporous SiO<sub>2</sub> support, the resulting materials were applied in the continuous hydroformylation of ethylene. Ethylene was used as the alkene feed as possible C<sub>6</sub> aldol products exhibit considerably higher volatility than the C<sub>10</sub> aldol compounds that originate from the hydroformylation of 1-butene.

The results obtained are presented in Figure 4. It is clear that, after an initial activation period, the physisorbed catalysts showed stable performance over the testing period of 70 h on stream without major deactivation. The reaction conditions ( $p=20$  bar,  $T=80^\circ\text{C}$ ) and a relatively low ethylene partial pressure in the feed gas were set with respect to a preferably low degree of conversion, which minimizes the probability of aldol product formation. However, also in this case, postreaction headspace-GC-MS analysis of the spent catalytic materials revealed the presence of C<sub>6</sub> aldol compounds to a significant extent. The main signal in the chromatogram depicted in Figure 5 can be attributed to 2-methyl-2-pentenal, and further signals stem from propanal and the hydrogenated C<sub>6</sub> aldol derivative 2-methylpentanal. Again, no aldol addition compounds were detected, which suggests that the formation of aldol condensation products seems to be highly favored under the reaction conditions applied.

It might be quite surprising that the relatively low-boiling C<sub>3</sub> aldehyde can be detected postreaction inside the macroporous catalyst material as its vapor pressure should be high enough to exclude condensation. However, as 2-methyl-2-pentenal condensed under the reaction conditions, the amount of



**Figure 4.** Conversion over time in ethylene hydroformylation using Rh-1 (◆) and Rh-2 (■) complexes on macroporous Trisopor 423; parameters:  $m_{\text{cat}} = 2.3$  g,  $m_{\text{Rh}} = 0.2$  wt%,  $L/\text{Rh} = 5$ ,  $T = 80$  °C,  $p = 20$  bar,  $p_{\text{ethylene}} = 1.0$  bar,  $p_{\text{H}_2} = p_{\text{CO}} = 9.5$  bar, residence time = 30 s.



**Figure 5.** Headspace-GC-MS analysis of Rh-1 (—) and Rh-2 (---) catalyst materials on macroporous  $\text{SiO}_2$  support after continuous hydroformylation of ethylene for 70 h. The main signals are attributed to propanal, 2-methyl-2-pentenal, and 2-methylpentanal, respectively.

propanal detected by headspace-GC-MS possibly derived from the dissolved compound in condensed  $\text{C}_6$  aldols.

In addition to simply weighing the catalyst materials before and after the reaction, the amount of high-boiling compounds accumulated in the pores was quantified by using thermogravimetric (TG) analysis. The difference in relative mass loss between the catalyst materials before and after use in the continuous gas-phase experiment was attributed to the mass increase caused by high-boiling products and compounds dissolved therein. The results obtained from TG measurements are summarized in Table 2 together with the mass increase determined by weighing and results from the catalytic experiments for comparison.

The increases of catalyst mass determined by TG analysis and weighing were of the same order of magnitude, even though the  $\Delta m$  values obtained from TG measurements were in general somewhat smaller, in particular for the Rh-1 based

**Table 2.** Summary of the catalytic results and catalyst mass increases determined by weighing and TG analysis. Degrees of conversion are related to the linear alkene substrate, and TOF values are in  $\text{mol}_{\text{aldehyde}} \text{ per mol}_{\text{Rh}} \text{ per hour}$ .

Catalyst material	Substrate	$\Delta m_{\text{weighing}}$ [%]	$\Delta m_{\text{TG}}$ [%]	$X_{\text{alkene}}$ [%]	TOF [ $\text{h}^{-1}$ ]
Rh-1/silica100 <sup>[a]</sup>	1-butene	5.2	3.0	5.1	90.5
Rh-2/silica100 <sup>[a]</sup>	1-butene	28.6	28.1	47.3	750.7
Rh-1/Trisopor423 <sup>[b]</sup>	ethylene	2.6	1.3	1.1	6.9
Rh-2/Trisopor423 <sup>[b]</sup>	ethylene	7.0	6.7	5.7	37.5
Rh-2/Trisopor423 <sup>[a]</sup>	1-butene	3.0	2.6	4.2	66.3

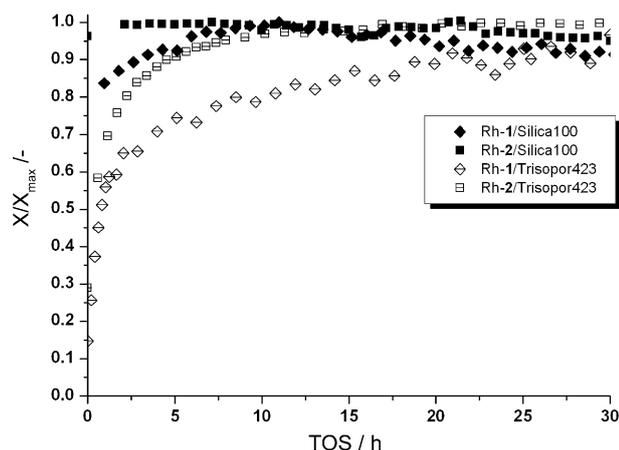
[a] Reaction conditions:  $T = 100$  °C,  $p_{\text{total}} = 10$  bar,  $p_{1\text{-butene}} = 1.8$  bar,  $p_{\text{H}_2} = p_{\text{CO}} = 4.1$  bar, residence time = 20 s; [b]  $T = 80$  °C,  $p = 20$  bar,  $p_{\text{ethylene}} = 1.0$  bar,  $p_{\text{H}_2} = p_{\text{CO}} = 9.5$  bar, residence time = 30 s.

materials. If we compare the Rh-1 and Rh-2-based catalysts, the latter showed a more pronounced mass increase, which corresponds to the higher catalytic activity. The higher catalytic activity clearly led to the enhanced formation of high-boiling compounds, which then remained to a certain extent in the pores of the catalyst support. This result was found for both ethylene and 1-butene and was also reflected by the peak intensities of the headspace-GC-MS analysis shown in Figures 3 and 5, respectively. Another explanation for the larger mass increase observed with Rh-2-based catalyst materials could be the higher Lewis acidity of the Rh complex as a result of the better  $\pi$ -accepting ability of ligand 2, which thereby promotes the aldol formation. Additionally, the influence of the support porosity was substantial as the replacement of silica 100 by Trisopor 423 while using the same Rh-2 catalyst complex in the continuous hydroformylation of 1-butene under identical reaction conditions leads to a significantly lower mass increase accompanied by a drastic decrease in catalyst activity (compare entries 2 and 5; additional details can be found in the Supporting Information). Following these investigations, the extent of pore filling with aldol and other high-boiling compounds during the course of the catalytic reaction seems to depend on a) the activity/nature of the immobilized catalyst species, b) the porosity/texture of the  $\text{SiO}_2$  support, and c) the vapor pressure of possible aldol compounds.

### Analysis of the start-up behavior

A comparison of the start-up behavior of the tested catalyst systems, that is, the development of the degree of conversion,  $X$ , within the first hours of time on stream, revealed that stable operation was reached after different times, which depended on the catalyst complex and support material. The maximum degree of conversion,  $X_{\text{max}}$ , was obtained almost spontaneously for Rh-2/silica100, whereas an activation behavior was observed for all other systems (Figure 6). In particular, the macroporous  $\text{SiO}_2$ -based catalysts showed pronounced activation periods, taking up to 15 and 30 h for Rh-1 and Rh-2 on Trisopor 423 to reach the maximum conversion.

For the case of steady-state operation at maximum conversion, the presence of a thermodynamic equilibrium between



**Figure 6.** Relative degree of conversion ( $X/X_{max}$ ) over time on stream for Rh-1 ( $\blacklozenge$ ) and Rh-2 ( $\blacksquare$ ) on silica 100 and the same catalyst complexes on Trisopor 423 (open symbols). Reaction parameters are given in the caption of Figures 1 and 4, respectively.

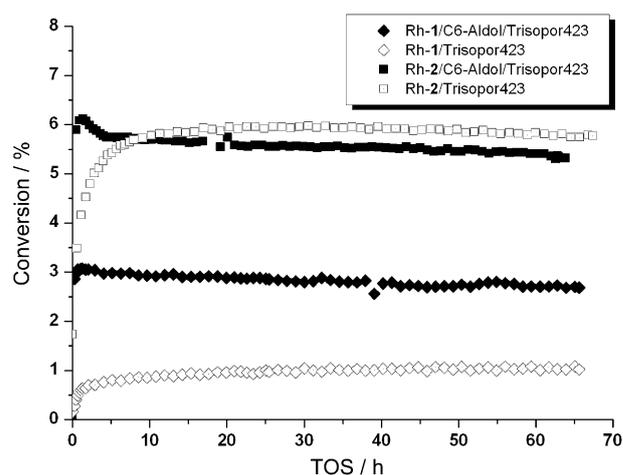
the condensation and evaporation of aldehyde and aldol products inside the porous catalysts is assumed. It takes longer to reach this equilibrium state if a macroporous instead of micro-/mesoporous support is used. This is because of the lower capillary pressure and generally lower degree of conversion characteristic of these catalytic materials. As a consequence, lower amounts of aldehyde and aldol products are formed during a certain time interval, which thus extends the time on stream needed to reach the maximum conversion.

### Catalyst behavior with aldol doping

To prove that the physisorbed catalyst species are dissolved by a condensed product phase in the pores of the support during the course of the continuous hydroformylation reaction, catalyst materials were prepared with a defined amount of 2-methyl-2-pentenal deliberately added during catalyst preparation. According to the mass increase determined by weighing the spent materials after 70 h on stream, 2.6 and 7.0 wt% of 2-methyl-2-pentenal were used as the supported liquid on Trisopor 423 to dissolve the Rh-1 and Rh-2 complexes, respectively, right from the beginning of the catalytic experiment. These amounts correspond to a theoretical degree of pore filling of 3 and 10 vol.% in relation to the total pore volume of the support. We subjected these materials to continuous hydroformylation of ethylene, and a very similar maximum conversion was obtained as in the case of the purely physisorbed catalyst complex for the Rh-2-based system (Figure 7).

In the case of Rh-1/Trisopor423 doped with 2-methyl-2-pentenal, the degree of conversion was higher than that of the system without  $C_6$  aldol. This result might be attributed to an insufficient dissolution of the Rh catalyst complexes in the aldol phase generated at a low degree of conversion, whereas it is assumed that all catalyst complexes are dissolved if 2-methyl-2-pentenal is added during the catalyst preparation.

The major difference between the systems with and without added 2-methyl-2-pentenal is, however, that no activation

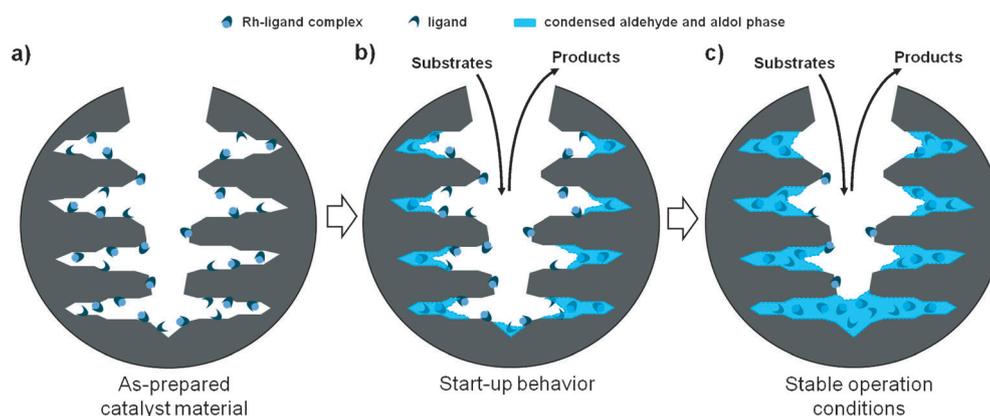


**Figure 7.** Conversion over time in ethylene hydroformylation using Rh-1 ( $\blacklozenge$ ) and Rh-2 ( $\blacksquare$ ) immobilized in 2-methyl-2-pentenal on Trisopor 423. 2-Methyl-2-pentenal was added in the catalyst preparation prior to catalytic reaction; parameters:  $m_{cat} = 2.36$  g (Rh-1) and 2.46 g (Rh-2),  $m_{Rh} = 0.2$  wt%,  $L/Rh = 5$ ,  $m_{2\text{-methyl-2-pentenal}} = 2.6$  wt% (Rh-1) and 7.0 wt% (Rh-2),  $T = 80$  °C,  $p = 20$  bar,  $p_{ethylene} = 1.0$  bar,  $p_{H_2} = p_{CO} = 9.5$  bar, residence time = 30 s. The results from Figure 4 (without 2-methyl-2-pentenal) are plotted for comparison (gray).

period is detected if the applied catalyst complexes are already dissolved in the  $C_6$  aldol product during catalyst preparation. In other words, by the addition of a particular amount of aldol product prior to the hydroformylation reaction, the catalytic materials start in the same state that a purely physisorbed system would reach only after several hours time on stream. These findings confirm the assumption that the homogeneous hydroformylation reaction indeed proceeds in liquid aldol products inside the porous support. As the filling of the pores with high-boiling compounds is supposed to be a dynamic process, a model can be developed based on the experimental results that describes the start-up behavior of purely physisorbed catalysts.

### Pore filling model

Based on the experimental results described above, the assumed dynamic process of pore filling with condensed aldol (and other high-boiling) products at the beginning of a continuous gas-phase experiment with a purely physisorbed catalyst complex is shown in Figure 8. According to the catalyst preparation, the initial material consists of the Rh catalyst complex, excess ligand, and traces of solvent from the material impregnation attached to the support surface (Figure 8a). On application of the reaction conditions, the catalytic production of aldehydes starts and with that—probably catalyzed by acidic silanol groups at the support surface—the consecutive formation of aldol products. As a result of their low volatility and the capillary pressure that exists in the porous network, these higher boiling products condense to some extent inside the pores of the support. According to classical pore condensation behavior, the micropores are filled first followed by the larger pores. The condensed aldol phase then dissolves the initially physisorbed ligand-modified Rh complex to provide a liquid



**Figure 8.** 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.

reaction phase for supported homogeneous catalysis (Figure 8b). Herein, the Rh species are supposed to behave similarly to that if the reaction takes place in a classical organic solvent, which shows the same *n/iso* selectivities. As the share of the dissolved catalyst molecules is still low at the beginning of a long-term experiment, the initial degree of conversion is low if macroporous supports are used. As the catalytic reaction proceeds, more aldehyde and aldol are formed, which in turn condense within the pores until a thermodynamic equilibrium between condensation and evaporation is reached under the conditions applied. From this point on, the degree of pore filling remains constant at a level that is characteristic for a given set of reaction parameters.

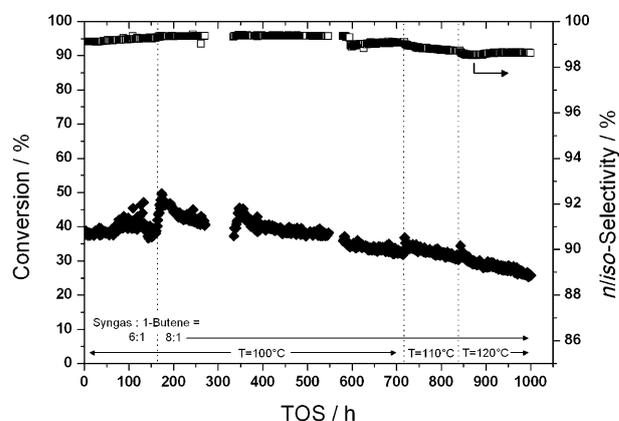
From the continuous hydroformylation experiments of ethylene using macroporous Trisopor 423 as the support, it can be concluded that the start-up/pore-filling period described above takes several hours. In the final state, that is, after the pore filling has reached equilibrium and a defined share of the pore volume is filled with condensed high-boiling compounds, steady-state operation is achieved under the reaction conditions applied (Figure 8c). Notably, it might be possible that some organometallic complexes remain undissolved on the support inner surface if the final degree of pore filling is at a relatively low level. This might explain the lower catalytic activity found in the case of Rh-1/Trisopor423 compared to the same system in which a predefined amount of 2-methyl-2-pentenal was added during catalyst preparation (Figure 7).

In such cases in which the aldol product is used explicitly for the immobilization of the Rh complex prior to the catalytic reaction, a particular degree of pore filling is already present in the as-prepared material. This starting point significantly shortens the dynamic process of (additional) pore filling under the reaction conditions. The equilibrium between the condensation and evaporation of high-boiling compounds is reached within a shorter time on stream.

### Long-term stability experiment

To study the long-term stability of catalyst materials obtained as described by dissolving Rh complexes in supported, high-

boiling reaction products, the Rh-2/silica100 material was subjected to a continuous gas-phase hydroformylation of an industrial  $C_4$  feedstock. This feed consists of 28% 1-butene, 44% 2-butenes,  $\leq 0.1\%$  *iso*-butene, and 28% inert butanes. The catalytic experiment was performed at Evonik Industries AG, Marl, Germany. The conversion over time is depicted in Figure 9, which shows highly active and selective catalyst operation for 1000 h on stream under the applied optimized conditions. At a high syngas/butene ratio of 8



**Figure 9.** Conversion (related to all butenes) over time in continuous gas-phase hydroformylation of industrial  $C_4$  feedstock using Rh-2/silica100 catalyst material. Parameters:  $m_{\text{cat}} = 12.0$  g,  $m_{\text{Rh}} = 0.2$  wt%,  $L/\text{Rh} = 10$ ,  $T = 100$ – $120$  °C,  $p = 10$  bar,  $p_{\text{butenes}} = 1.6$  bar (1.3 bar),  $p_{\text{butanes}} = 0.6$  bar (0.5 bar),  $p_{\text{H}_2} = p_{\text{CO}} = 3.9$  bar (4.1 bar) before (and after) variation of the syngas/butene ratio from 6 to 8 after 170 h on stream, residence time = 48 s (43 s).

(parameter change after 170 h on stream) the catalyst showed a typically high regioselectivity of 99.4% to linear pentanal, comparable to the results obtained with pure 1-butene feedstock (Figure 2).

The initial degree of conversion of 38% was well maintained within the first 170 h on stream. After increasing the syngas/butene ratio, the catalyst activity increased almost instantaneously, probably as a result of the higher syngas availability in the liquid catalyst phase. We attribute this rather unexpected observation to the assumption that mass transfer limitations might play a role in this particular case because of the relatively high degree of pore filling with aldol products (45 vol.%). Regarding the comparative catalyst systems in which pore filling is below 10 vol.% and thin films of aldol provide a high exchange surface, similar syngas/alkene variation resulted in a more common catalyst behaviour, which resulted in a lower catalyst activity for a higher syngas/alkene ratio (see Support-

ing Information). For the continuous  $C_4$  hydroformylation, slight deactivation was observed over a prolonged reaction time. The extent of this deactivation behavior is comparable to that observed for Rh-2/silica100 with a pure 1-butene feed. A temperature variation to 110 and 120 °C resulted in slightly lower *n/iso* selectivities and more pronounced catalyst deactivation. Even though the extraordinary long-term stability of a comparable SILP system<sup>[10]</sup> was not achieved, the observed behavior is quite remarkable for an initially purely physisorbed catalyst complex with a labile diphosphite ligand such as **2**. One possible explanation for deactivation might be the formation of water as a side-product of the aldol reaction. During the long-term test, considerable amounts of water are formed in the pores, which possibly lead to the gradual hydrolysis of **2** over time.

In addition, inductively coupled plasma (ICP) measurements of spent catalyst materials often revealed a decreased Rh content, which was of the same order of magnitude as the loss of catalytic activity observed during the catalytic runs. This loss of Rh is probably caused by liquid entrainment of the condensed aldol phase from the support over the duration of a continuous experiment.

## Conclusions

Catalytic materials comprising Rh complexes with sulfoxantphos (**1**) and benzopinacol-based ligands (**2**), Rh-1 and Rh-2, respectively, dispersed on the internal surface of porous  $SiO_2$  materials have been prepared and successfully tested in the continuous gas-phase hydroformylation of short-chain alkenes. The observed regioselectivities to the linear aldehyde were 97 and 99.5%, respectively, which are comparable to those typically obtained in classical liquid-phase and supported ionic-liquid-phase (SILP) catalysis. A significant mass increase of up to 30% was revealed by weighing the catalytic materials after the reaction in the case of Rh-2/silica100. By using headspace-GC-MS analysis, this increase in catalyst mass could be attributed to high-boiling compounds that were generated during the hydroformylation process itself. Herein, the aldol condensation products were clearly assigned as the main components. Dissolved in a condensed phase of high-boiling compounds inside the pores of the supporting material, the catalytically active species operate in a homogeneous fashion. A model that explains the process of pore filling during the catalytic reaction and possible differences in the start-up behavior of the tested catalyst materials has been presented. The amount of condensed high-boiling compounds was found to depend on the catalyst activity and porosity of the applied  $SiO_2$  support. The catalysts were remarkably stable under the optimized conditions, but long-term experiments (up to 1000 h) still revealed some decay in the system activity. This finding distinguishes these product-supported systems from classical SILP catalysts, in which the presence of an ionic liquid film provides a more robust stabilizing liquid phase for the active Rh complex.

## Experimental Section

### Chemicals

$Rh(CO)_2(acac)$  (*acac* = acetylacetonate), methanol, and dichloromethane (HPLC grade) were purchased from Sigma-Aldrich and used without further purification. The sulfoxantphos ligand **1** was synthesized by sulfonation of 9,9-dimethyl-4,5-bis(di-*tert*-butylphosphino)xanthene (Sigma-Aldrich) according to a literature procedure.<sup>[14]</sup> The benzopinacol ligand 2,2'-[(3,3'-di-*tert*-butyl-5,5'-dimethoxybiphenyl-2,2'-diyl)bis(oxy)]bis-(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane) (**2**) was supplied by Evonik Industries AG, Marl, Germany. Silica gel 100 (63–200  $\mu m$ ) was purchased from Merck, and Trisopor 423 (100–200  $\mu m$ ) from VitroBio GmbH. For the long-term stability experiment silica gel 100 (200–500  $\mu m$ ) was used. The  $SiO_2$  materials were pretreated at 600 °C for 18 h before use in catalyst preparation. 1-Butene (99.5%), ethylene (99.95%), CO (99.97%), and  $H_2$  (99.999%) were purchased from Linde AG. The industrial  $C_4$  feedstock was provided by Evonik Industries AG and contained 28% 1-butene, 44% 2-butenes,  $\leq 0.1\%$  iso-butene, and 28% inert butanes. 2-Methyl-2-pentenal (97%) was purchased from Sigma-Aldrich.

### Catalyst preparation

All syntheses were carried out using standard Schlenk techniques under Ar (99.999%).  $Rh(CO)_2(acac)$  was dissolved in methanol or dichloromethane, for the reaction with **1** or **2**, respectively, and stirred for 5 min. Ligand **1** or **2** was added in a fivefold molar excess (ligand/Rh = 5) dissolved in methanol or dichloromethane, respectively, and the resulting solution was stirred for 5 min. In the long-term stability experiment, a tenfold molar excess of **2** (ligand/Rh = 10) was used. After addition of the appropriate amount of calcined silica 100 or Trisopor 423 (see Supporting Information), 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 ( $1 \times 10^{-4}$  bar) overnight. In the case of aldol addition prior to catalysis, 2-methyl-2-pentenal was mixed with the Rh-1 and Rh-2 solution, respectively, before addition of the solid support. No drying under high vacuum was performed for these catalytic materials (for details see Supporting Information).

### Catalytic experiments

The reaction setup applied in our laboratories for continuous gas-phase hydroformylation comprised a fixed-bed reactor, upstream feed dosing, evaporation and mixing, downstream pressure regulation, and online GC. The entire rig was heated by using electric heating devices. The catalyst material was filled into a tubular reactor and purged three times with He at room temperature. The rig was pressurized with He and left under pressure for 15 min while monitoring the pressure. If no pressure drop was observed, the reactor was heated to the reaction temperature under He pressure. After adjustment of the molar flows, the feed gas (alkene and syngas) was allowed to enter the reactor. The alkene substrate was fed into the rig by using an HPLC pump, and syngas was dosed by using mass-flow controllers. Evaporated alkene was combined with the preheated reaction gases in a mixing unit, which was filled with glass beads to ensure proper mixing and isothermal conditions. The gas mixture could then either enter the reactor or exit the system through a bypass. The reactor consisted of a stainless-steel tube (12 mm diameter, 500 mm length) equipped with

a porous frit for catalyst placement and a thermocouple to measure the inner reactor temperature. After the reactor unit, the gas mixture passed a 7  $\mu\text{m}$  filter to avoid contamination of the tubing with catalyst or solid particles. A backpressure regulator valve (Samson) was used to maintain the desired reaction pressure and outlet gas flow. After the regulator valve, the gas stream was split and a minor flow was passed through a 1 mL sampling loop mounted on an online GC (Agilent 7890A). Samples were taken at regular intervals by injecting the volume of the sampling loop through a six-port valve into the GC.

### Analysis

The product gas composition was monitored over time by using an online GC. An Agilent 7890A GC was equipped with a GS-GasPro capillary column (Agilent Technologies, length 30 m, inner diameter 0.32 mm) and a flame ionization detector (FID). Acquisition parameters: injector temperature 250 °C, split ratio 10:1, constant column flow 4.5 mL min<sup>-1</sup>, detector temperature 260 °C. Temperature profile: initial temperature 60 °C, hold time 2.5 min, heating to 200 °C at 40 °C min<sup>-1</sup>, hold time 4 min, total time 10 min. In the long-term stability experiment, an Agilent 6890 instrument equipped with a dimethylpolysiloxane-coated column (Agilent Technologies, length 50 m, inner diameter 0.2 mm, film thickness 0.5  $\mu\text{m}$ ) and an FID was used. Acquisition parameters: injector temperature 200 °C, split ratio 33.5:1, constant column flow 74 mL min<sup>-1</sup>, detector temperature 250 °C. Temperature profile: initial temperature 50 °C, hold time 15 min, heating to 200 °C at 25 °C min<sup>-1</sup>, hold time 40 min, total time 61 min.

Headspace-GC-MS analysis was performed by using a Varian 450-GC combined with a Varian 220-MS. A Combi PAL GC autosampler (CTC Analytics) equipped with heatable agitator was used for sample injection. Spent catalyst (0.5 g) was put into a headspace vial and heated to 130 °C for 15 min. Gas samples of 500  $\mu\text{L}$  were injected by using a preheated syringe (130 °C). A FactorFour VF-5 MS capillary column (Varian, length 30 m, inner diameter 0.25 mm) was used for compound separation. The ionization mode was set to electron impact (EI). Parameters: injector temperature 250 °C, split ratio 10:1, constant column flow 1.0 mL min<sup>-1</sup>. Temperature profile: initial temperature 40 °C, hold time 3.0 min, heating to 100 °C at 5 °C min<sup>-1</sup>, hold time 10.5 min, heating to 200 °C at 10 °C min<sup>-1</sup>, hold time 0.5 min, total time 36 min.

The mass loss of the catalytic materials was measured by TG analysis by using a Setsys 1750 Cs Evolution (Setaram Instrumentation) instrument equipped with a 350  $\mu\text{L}$  quartz crucible. The TG signal was monitored over the following temperature program: initial temperature 30 °C, He carrier gas flow 200 mL min<sup>-1</sup>, hold time 10 min, reduce He carrier gas flow to 50 mL min<sup>-1</sup>, hold time 2 min, heating to 900 °C at 10 °C min<sup>-1</sup> and carrier gas flow 50 mL min<sup>-1</sup>, hold time 90 min, cooling to 30 °C at 30 °C min<sup>-1</sup> and carrier gas flow 200 mL min<sup>-1</sup>, final temperature 30 °C, final carrier gas flow 5 mL min<sup>-1</sup>.

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