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Catalyst recycling *via* specific non-covalent adsorption on modified silicas†‡

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This article describes a new strategy for the recycling of a homogeneous hydroformylation catalyst, by selective adsorption of the catalyst to tailor-made supports after a batchwise reaction. The separation of the catalyst from the product mixture is based on selective non-covalent supramolecular interactions between a ligand and the support. Changing the solvent releases the active catalyst back into the reactor and allows a subsequent batch reaction with the recycled active catalyst. For this purpose, the bidentate NixantPhos ligand has been equipped with a pyridine group. The corresponding rhodium pre-catalyst [Rh(Nix-py)(acac)] (acac = acetylacetonate) forms a very selective, active and highly stable catalyst, and able to reach a turnover number (TON) of 170 000 in a single run (reaction performed in nearly neat 1-octene, S/C ratio of 200 000, at 140 °C, 20 bars syngas pressure). Various commercially available supports have been explored in binding studies and recycling experiments. The end-capped silica-alumina performs the best so far with respect to ligand-adsorbing properties for the current purpose. Although this system has not been fully optimized, four recycling runs could be performed successfully.

Introduction

The efficient separation and subsequent recycling of homogeneous transition metal catalysts remains a topic that not only constitutes a scientific challenge but also has significant commercial relevance. Homogeneous catalysis facilitates an atom-economic synthetic approach in which all atoms of the reagents end up in the product. In addition, a high degree of tunability of the catalyst activity, chemoselectivity, regioselectivity and enantioselectivity can be achieved.[1] However, the lack of efficient recycling methodologies that can be applied on industrial scale currently restricts the use of homogeneous catalysis to the production of valuable fine-chemicals.[2] Standard industrial purification operations such as distillation, extraction, and filtration are often incompatible or at least limiting when employing temperature-, hydrolysis- or oxidation-sensitive molecular catalyst systems.

So far, several strategies for advanced catalyst recycling have been explored, which can be broadly grouped into two types. The first group links the active catalyst covalently to some kind of soluble or insoluble support and separation is accomplished by a (nano)filtration technique.[2,3] Various scaffolds have been used such as dendritic,[4] polymeric organic, inorganic, or hybrid supports.[5,6] The other type of recycling methodology is the selective partitioning of the catalyst from the reactants and products that can be achieved by employing two immiscible solvents in the separation step. An example of successful industrial implementation is the biphasic Ruhrchemie/Rhône-Poulenc process for the hydroformylation of propene.[7] Other biphasic systems such as supported aqueous phase catalysis,[8] fluorous biphasic catalysis,[9] and the use of (supported) ionic liquids[10] and supercritical fluids[11] have been reported.

Previously, we reported the use of a non-covalent, supramolecular host–guest anchoring strategy for the immobilization of homogeneous catalysts on silica supports with well-defined binding sites.[12] The supramolecular interaction between the binding motif tethered to the transition-metal catalyst and the binding site located on the support was sufficiently strong to enable catalyst immobilization and efficient catalyst recycling. The host–guest binding of the silica-supported systems was found to correspond well with the analogous systems in solution. Importantly, it was shown that the binding is fully reversible, and just changing the solvent allows the reuse of the support. The supramolecular host–guest immobilization was further developed for a Reverse-Flow Adsorption (RFA) reactor

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†This contribution is dedicated to Professor David J. Cole-Hamilton on the occasion of his 65th birthday.
‡Electronic Supplementary Information (ESI) available: Ligand synthesis, experimental details and additional NMR spectra. See DOI: 10.1039/c2dt32047a
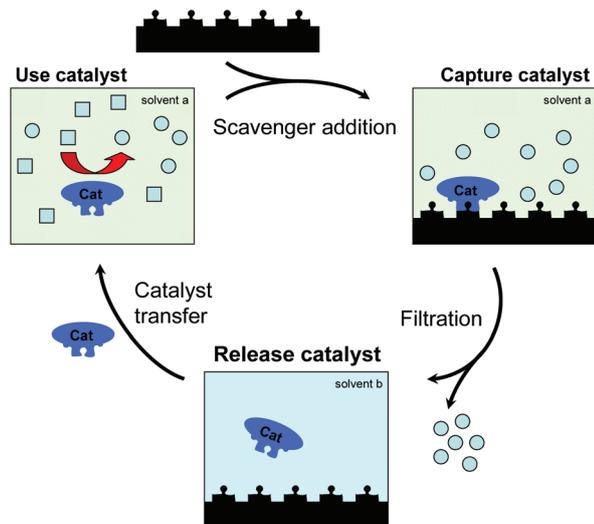
Fig. 1 Catalyst recycling *via* a reversible catalyst adsorption strategy using non-covalent interactions.

Scheme 1 Rhodium catalyzed hydroformylation of 1-octene leading to aldehyde products.

Scheme 2 Functionalization of NixantPhos (**1**) with a pyridyl function for reversible binding to Lewis and Brønsted acidic supports.

that integrates selective recovery and recycling of the homogeneous catalysts from the reactor effluent.[13] For this purpose the binding motif to adsorb the catalyst was adjusted such that the binding was weaker ($K_{ads} = 10^3$), and a complementary ligand-binding motif was covalently attached to the silica support. This enables a one-step adsorption of both the transition metal complex and the excess ligand. Importantly, the metal complex remained intact during the adsorption and reaction conditions, which is crucial for efficient catalyst recycling. A continuous process-integrated recycling of a rhodium-catalyst for asymmetric hydrogenation of methyl acetamidoacrylate and asymmetric hydrosilylation of acetophenone has been demonstrated.[13] The system is still far from perfect as the adsorption process is limited by adsorption kinetics. As a result, only a few percent of the binding sites on silica could be effectively used. Also, in this non-optimized system, a large part of the catalyst resides on the adsorption bed and is therefore not used. In addition, implementation of this concept also requires a significant investment. Based on these results and arguments we wondered if we could apply similar adsorption strategies for batchwise reactions.

We decided to investigate this catalyst recycling strategy for the industrially important Rh-catalyzed hydroformylation. The concept, displayed in Fig. 1, implies that after a batch reaction the catalyst is selectively scavenged by the tailor-made support using non-covalent binding. After separation of the catalyst from the product mixture, the adsorption bed is washed with a different (more polar) solvent to disrupt the supramolecular interactions, thus releasing the catalyst from the bed. Reintroduction of the catalyst into the reactor and addition of new reactants (1-octene and syngas) allows the subsequent catalytic run with the recycled active catalyst. Here we report the use of homogeneous Rh-catalysts tethered with a support-specific binding motif for the hydroformylation of 1-octene under homogeneous conditions (Scheme 1). Various commercially
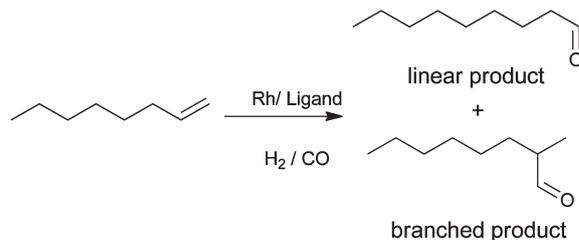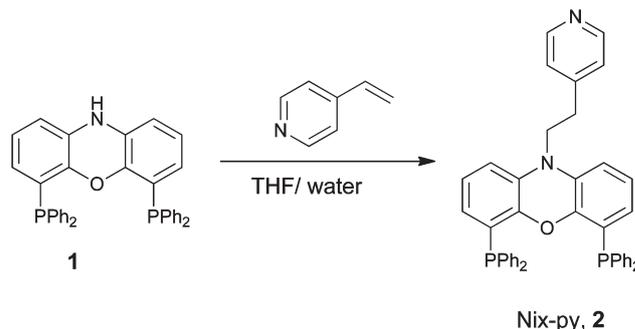
available supports with Lewis and Brønsted acidic sites have been investigated in combination with a pyridyl-functionalized NixantPhos (**2**) ligand. Two supports were selected for further application in the hydroformylation reaction of 1-octene and used in several consecutive reactions.

Results

XantPhos-type ligands are excellent ligands for Rh-catalyzed hydroformylation.[14] The combination of the large bite-angle and the rigidity of the backbone allows α-olefins to be hydroformylated with high linear/branched ratios. Within the Xant-Phos-family, NixantPhos (**1**) is most readily modified and functionalized at the N–H and here we performed a hydroamination reaction using 4-vinyl pyridine under basic conditions, introducing a pyridine moiety in nearly quantitative yield (**2**, Nix-py, see Scheme 2).

Catalyst Rh(**2**) was first evaluated in the hydroformylation of 1-octene under batch conditions and compared to the performance of the Rh/XantPhos catalyst (see Table 1). Both systems display similar activity and selectivity, which implies that the presence of the pyridyl moiety has no adverse effect on the hydroformylation reaction. Clearly, the reaction can also be run at more elevated temperatures (140 °C) with a high S/C ratio (200 000), confirming that Rh(**2**) is sufficiently stable to reach high turn-over numbers (TON of 170 000, see entry 3, Table 1). Based on these experiments the catalyst recycling experiments were designed to run in nearly neat 1-octene. The

Table 1 Hydroformylation of 1-octene[a]

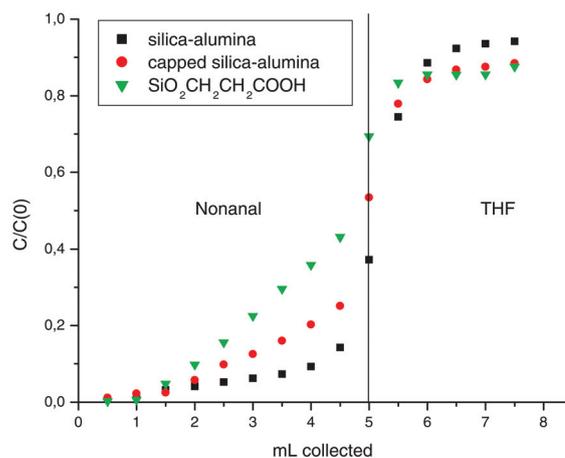| Entry	Ligand	S/C[e] ratio	Additive	Time (h)	Conv. (%)	Linear ald (%)	Branched ald (%)	Isomers (%)	l : b	TOF[c] (h^{-1})
1	XantPhos	10 000	—	23	92.2	93.8	2.7	3.5	35.0	406
2	Nix-py	10 000	—	23	89.6	93.6	2.4	4.0	38.9	386
3[b]	Nix-py	200 000	5 mL THF	1.8	87.1	91.5	2.3	6.1	39.0	33 137
4	Nix-py	10 000	SiO$_2$/Al$_2$O$_3$[d]	21	22.0	89.0	2.7	8.3	32.8	103

[a] 80 °C, 20 bars (H$_2$/CO 1 : 1), 50 mL 1-octene, 7.8 mg Rh(acac)(CO)$_2$, L/Rh = 5. [b] 140 °C, 20 bars (H$_2$/CO 1 : 1), 45 mL 1-octene, 0.32 mg Rh(acac)-(CO)$_2$, L/Rh = 5. [c] Turn-over frequency defined as mol$_{aldehyde}$/mol$_{catalyst}$ × hour. [d] 1 g uncapped silica-alumina was added to the reaction mixture. [e] S/C ratio = substrate to catalyst ratio.

Table 2 Adsorption constant (K_{ads}) and number of binding sites for the adsorption of **2** to different solid supports

| Entry	Support	K_{ads} (M^{-1}) nonanal	Number of binding sites (mmol g^{-1})	K_{ads} (M^{-1}) THF
1	(SiO$_2$)$_n$–CH$_2$CH$_2$COOH	7.0×10^2	0.1	n.d.
2	(SiO$_2$)$_n$–CH$_2$CH$_2$CH$_2$–NHC(O)NH(p-chloro)-phenyl	<1	—	n.d.
3	γ-Alumina	<1	—	n.d.
4	Silica-alumina capped	2×10^3	0.3	<5
5	Silica-alumina	4×10^5	0.23	<5
6	Silica-alumina	8.5×10^3 (5% THF)	0.3	n.d.
7	Silica-alumina	6.4×10^3 (15%THF)	0.3	n.d.

Fig. 2 Flow experiments using 2.5 mM **2** and non-capped silica-alumina (200 mg) (black), end-capped silica-alumina (200 mg) (red) and carboxylic acid silica (300 mg) (green). After passing 5 mL nonanal containing **2** (0.5 mM) over the column, the solvent was changed to pure THF and the flow was reversed. Samples of 0.5 mL were collected. Amounts of **2** have been scaled by dividing the cumulative amount measured ($C_{sample} \times V_{sample}$) by the initial concentration ($C(0) \times V_{total}$).

recycling experiments have been performed at lower reaction temperatures (80 °C) and substrate/catalyst ratio (S/C = 10 000). Furthermore, THF and nonanal, the principal product obtained from hydroformylation, were used as solvents in the binding studies.

The sorption characteristics of **2** were studied by determining the adsorption constants (K_{ads}) of **2** to different solid supports that contain either (1) only Brønsted acid sites ((SiO$_2$)$_n$–CH$_2$CH$_2$COOH), (2) Lewis acid sites (neutral γ-alumina) or (3) both (silica-alumina).[15] The results are collected in Table 2. The adsorption constant (K_{ads}) of **2** has been determined by fitting the data, obtained by direct titration, with a (modified) Langmuir-isotherm.[16] Interestingly, there appears to be no affinity of **2** for neutral γ-alumina while a very high binding constant for the untreated silica-alumina was found (compare entries 3 and 5). Capping the silica-alumina support with dimethyldimethoxysilane to convert the silanol groups into unreactive methyl end-groups reduces the binding constant by a factor of 100 while the accessible number of binding sites remains the same. A similar drop in adsorption constant was obtained for the untreated silica-alumina if 5% or 15% THF was added to the nonanal solution during the adsorption experiment. This shows that limited amounts of desorption-solvent THF affect the binding to a limited extent, but under these conditions the adsorption is still sufficient for selective catalyst removal. The adsorption strength of **2** to capped silica-alumina corresponds well to the optimum binding strengths

reported by De Haan et al. for adsorption/desorption processes in RFA.[17]

To study the adsorption/desorption in more detail, flow experiments were conducted wherein a stock solution of 2.5 mM **2** in nonanal was passed over a packed column. The concentration of the ligand after the bed was determined using UV-Vis spectroscopy. After passing 5 mL of the stock solution over the column the flow was reversed and THF was used as the desorption solvent for the ligand and the efficiency was determined by measuring the concentration of **2**. Fig. 2 displays the flow experiments employing the different supports. The retention of **2** on the support is in line with the adsorption constants in Table 2, with the ligand **2** strongly adsorbed on silica-alumina and fortunately also being efficiently desorbed. As silica-alumina showed the best retention-and-release performance for **2**, we studied the use of this combination in more detail.

Increasing the amount of solid support resulted in a better retention of **2** (Fig. 3). Leaching of **2** (measured at 4.5 mL of stock solution passed) was reduced from 14% for 200 mg to 4% for 400 mg silica-alumina. In addition, desorption with
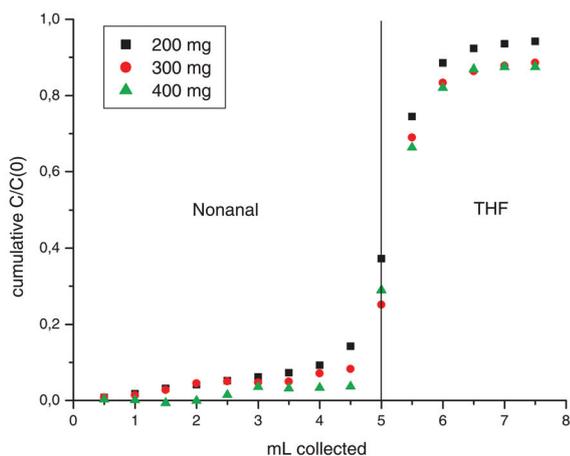
Fig. 3 Flow experiments using 2.5 mM **2** with various amounts of silica-alumina at a constant flow-rate (0.25 mL min⁻¹). After passing 5 mL nonanal containing **2** (0.5 mM) over the column, the solvent was changed to pure THF and the flow was reversed. Samples of 0.5 mL were collected. Amounts of **2** have been scaled by dividing the cumulative amount measured ($C_{sample} \times V_{sample}$) by the initial concentration ($C(0) \times V_{total}$).
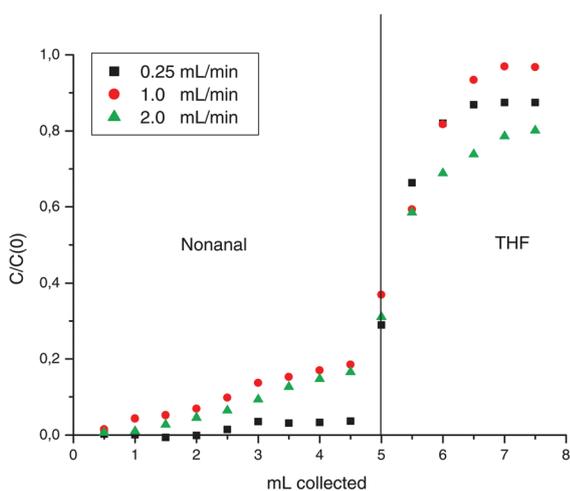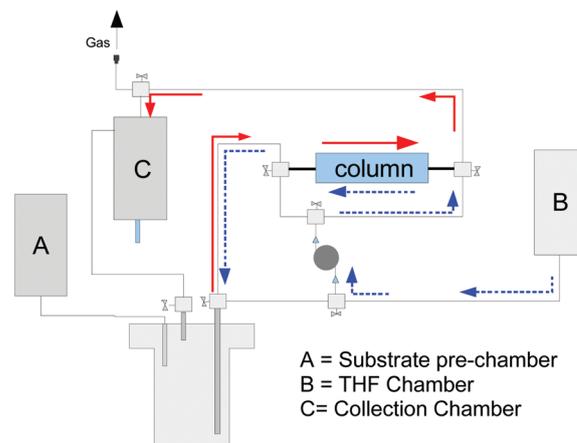

Fig. 5 Reactor setup and separation column. The red arrows indicate the flow-direction of the reaction mixture (adsorption) and the blue arrows indicate the flow of the THF (desorption).

Fig. 4 Flow experiments using 2.5 mM **2** at different flow-rates with a constant amount of silica-alumina (400 mg). After passing 5 mL nonanal containing **2** (0.5 mM) over the column, the solvent was changed to pure THF and the flow was reversed. Samples of 0.5 mL were collected. Concentrations have been scaled by dividing by the start concentration ($C(0)$). Amounts of **2** have been scaled by dividing the cumulative amount measured ($C_{sample} \times V_{sample}$) by the start concentration ($C(0) \times V_{total}$).

THF was not greatly affected and a high recovery of **2** was observed in all cases (87–93%). Changing the flow-rate of the solution revealed more insight into the kinetics of the sorption processes. From Fig. 4 it is clear that a lower flow rate and thus increased contact time greatly improves the retention of **2** to the support and reduces the leaching at 4.5 mL to 4% (compared to 18% for a flow rate of 2.0 mL min⁻¹), while also the desorption profile improves with a recovery of **2** of 87%.

For optimal recycling of the catalyst, the rhodium complex should remain in its active form to be efficiently used in the

subsequent runs. To probe a potential effect of the silica-alumina support on the hydroformylation results, the reaction was performed with the silica-alumina present in the reaction mixture. Entry 3 of Table 2 shows that the selectivity of the hydroformylation reaction is not affected, while the activity is significantly lower, probably due to (partial) physisorption or entrapment of the catalyst rather than actual deterioration of the system although we have no conclusive proof to exclude catalyst decomposition at this point.

Recycling experiments have been performed using the set-up as shown in Fig. 5 under very similar reaction conditions as in the batch reactions (Table 2). At all times during the re-cycling process the syngas pressure was kept at 20 bars and the conversion was kept below 90%. From preliminary experiments it was found that the retention of the catalyst to the adsorption-bed was improved when the reaction mixture was cooled to room temperature before pumping the reaction mixture over the absorber-bed. Unmodified silica-alumina (entry 5, Table 2) with high binding affinity was initially selected for further studies. The flow-rate during the adsorption and desorption process was kept constant at 0.5 mL min⁻¹.

The hydroformylation results using the unmodified silica-alumina are presented in Table 3. The first run shows the typical results expected from this rhodium complex, comparable with a Rh-catalyst bearing the non-functionalized NixantPhos ligand, but recycling experiments lead to partial erosion of catalyst performance in the three subsequent runs. The selectivity for the linear product remains high and substrate isomerisation only becomes significant in the last reaction. The activity drops substantially after each recycling procedure. Analysis of the collected effluent showed that the rhodium leaching is low, between 0.5 and 1.3%. These data strongly indicate that the Rh(**2**) catalyst is scavenged very well from the reaction mixture by the solid support, but that the active catalyst is either not efficiently desorbed or is deactivated by the support. Possibly, the catalyst resting state

Table 3 Recycle of the hydroformylation catalyst using silica-alumina[a]

Run	Time (h)	Conv. (%)	Linear ald (%)	Branched ald (%)	Isomers (%)	l:b	TOF[b] (h^{-1})	[Rh][c] mg L^{-1}	[P][c] mg L^{-1}
1	18	92.3	94	2.2	4.1	43.0	1134	0.16 (0.7%)	11.3 (11%)
2	18	64.5	93	2.2	4.6	41.8	797	0.13 (0.5%)	13.1 (13%)
3	19	62.5	91	2.4	6.3	38.6	732	0.32 (1.3%)	14.3 (14%)
4	19	25.6	81	2.6	15.8	31.8	269	0.16 (0.7%)	6.15 (8%)

[a] 90 °C, 20 bars (H$_2$/CO 1:1), 45 mL 1-octene, 5 mL THF, 3.1 mg Rh(acac)(CO)$_2$, S/Rh = 22 500, L/Rh = 5, 2.6 g SiO$_2$/Al$_2$O$_3$. [b] Turn-over frequency defined as mol$_{aldehyde}$/(mol$_{catalyst}$ × hour). [c] Concentration of rhodium and phosphorus in the collected product. Numbers in brackets are the percentage of initial concentration.

Table 4 Recycle of the hydroformylation catalyst using end-capped silica-alumina[a]

Run	Time (h)	Conv. (%)	Linear ald (%)	Branched ald (%)	Isomers (%)	l:b	TOF[b] (h^{-1})	[Rh][c] mg L^{-1}	[P][c] mg L^{-1}
1	18	90	92	2.1	5.7	43.3	1116	0.13 (0.6%)	14 (20%)
2	18	73	93	2.2	4.5	42.3	924	0.20 (0.8%)	11 (15%)
3	19	75	56	4.1	39.5	13.9	557	1.8 (7.4%)	13 (18%)
4	19	60	43	5.7	50.9	7.6	385	0.8 (3.5%)	8 (11%)
5	25	63	17	4.4	78.6	3.9	129	0.3 (1.3%)	8 (11%)
6	17	77	84	2.4	14.0	34.8	920	0.5 (2.1%)	25 (—)
7	18	61	92	2.3	6.1	40.4	768	0.3 (1.2%)	11 (—)
8	20	68	71	3.1	25.5	22.7	612	n.d.	n.d.

[a] 90 °C, 20 bars (H$_2$/CO 1:1), 45 mL 1-octene, 5 mL THF, 3.1 mg Rh(acac)(CO)$_2$, S/Rh = 22 500, L/Rh = 5, 2.6 g Aldrich Catalyst carrier SiO$_2$/Al$_2$O$_3$. [b] Turn-over frequency defined as mol$_{aldehyde}$/(mol$_{catalyst}$ × hour). [c] Concentration of rhodium and phosphorus in the collected product. Numbers in brackets are the percentage of initial concentration.

Table 5 Recycle of the hydroformylation catalyst using end-capped silica-alumina with one equivalent ligand added in every run[a]

Run	Time (h)	Conv. (%)	Linear ald (%)	Branched ald (%)	Isomers (%)	l:b	TOF[b] (h^{-1})	[Rh][c] mg L^{-1}
1	18	87	94	2.2	3.7	43.2	1107	<3 (<0.2%)
2	18	58	92	2.2	6.0	41.4	721	10 (0.6%)
3	18	56	91	2.2	6.6	41.0	688	13 (0.7%)
4	18	69	90	2.5	8.0	36.2	832	96 (5.3%)
5	18	37	45	4.7	50	9.6	18	27 (1.5%)

[a] 90 °C, 20 bars (H$_2$/CO 1:1), 45 mL 1-octene, 5 mL THF, 3.1 mg Rh(acac)(CO)$_2$, S/Rh = 22 500, L/Rh = 5, 2.6 g Aldrich Catalyst carrier SiO$_2$/Al$_2$O$_s$. [b] Turn-over frequency defined as mol$_{aldehyde}$/(mol$_{catalyst}$ × hour). [c] Concentration of rhodium in the collected product. Numbers in brackets are the percentage of initial concentration.

[Rh(**2**)H(CO)$_2$] reacts with Brønsted acidic sites of the support, producing cationic rhodium complexes.[6b] To circumvent these problems the end-capped silica-alumina, lacking reactive (acidic) OH-groups, was subsequently investigated in the catalyst recycling.

The hydroformylation results using the end-capped silica-alumina are presented in Table 4. Again, the first reaction showed the typical results expected from a Rh(NixantPhos) complex, with high activity and selectivity for the linear aldehyde obtained. Upon recycling, the catalyst activity gradually drops from a TOF of 1116 to 557 in the first four runs. Also the selectivity towards linear aldehyde drops significantly in the third run. The linear/branched ratio in the fifth run is close to the ligand-free hydroformylation system, suggesting that the ligand leached from the reactor. This is also confirmed by the phosphorus leaching data in Table 4. Extra ligand was added to the reaction mixture in the sixth run and indeed the hydroformylation activity and selectivity were almost completely restored to initial levels in the seventh run. Although the retention of the ligand was not ideal, these results show the proof-of-principle of a reversible supramolecular catalyst scavenging technology.

With the knowledge that part of the ligand is lost during the recycling, the recycling experiments were performed with an additional equivalent ligand in each batch reaction. As can be seen from Table 5, four successful recycling experiments were performed where the catalyst was taken out of the reactor, passed over an adsorption bed and reintroduced into the reactor. The activity dropped slightly in the second run but remained stable until the fifth run. Importantly, the selectivity can be retained in the first four reactions under these conditions, but is almost completely lost in the fifth run. Rhodium analysis of the effluent (see Table 5) and the rhodium levels in the autoclave (27% of the initial amount) show that a significant amount of rhodium still resides on the catalyst scavenger bed. Although the properties of the catalyst

are lost in the fifth run, these results clearly show that the combination of batchwise reactions and catalyst scavenging using a selective adsorbent is very promising. Further research should focus on optimization of selective adsorbent materials.

Conclusions

In this contribution we have demonstrated a new strategy for the recycling of a homogeneous hydroformylation catalyst, by selective adsorption of the catalyst to tailor-made supports after a batchwise reaction. The binding of the catalyst is based on selective non-covalent interactions between ligand and support. For this purpose, the NixantPhos ligand has been functionalized with pyridine groups. The corresponding Rh catalyst is very selective, active and highly stable, reaching a TON of 170 000. Various commercially available supports were explored, with the end-capped silica-alumina showing the best results of this study with respect to ligand-adsorbing properties. The related unfunctionalized analogue binds better, but this material accelerates catalyst deactivation during the recycling experiment. Under optimized conditions, four successful recycling experiments were performed (at 90 °C, 20 bars syngas pressure, substrate/catalyst ratio 22 500). The activity dropped slightly in the second run but remained stable until the fifth run after which the activity and selectivity were lost. Further optimization is required before such recycling strategies can be efficiently applied for commercial processes, but proof-of-concept for this supramolecular scavenging strategy is demonstrated by the experiments outlined in this paper.

Experimental

General procedures

Unless stated otherwise, reactions were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. THF was distilled from sodium benzophenone ketyl, methanol was distilled from CaH_2, and toluene was distilled from sodium, all under a nitrogen atmosphere. NMR spectra were measured on a Bruker AV 400 (^{1}H: 400 MHz, ^{31}P-{^{1}H}: 162 MHz and ^{13}C{^{1}H}: 101 MHz) at room temperature. Chemical shifts are reported in ppm and are given relative to tetramethylsilane (^{1}H and ^{13}C{^{1}H}) or 85% H_3PO_4 (^{31}P{^{1}H}) as external standards. High resolution mass spectra (HRMS) were recorded using FAB$^+$ ionization on a JEOL JMS SX/SX 102A four-sector mass spectrometer with 3-nitrobenzyl alcohol as the matrix. Rhodium and phosphorus analyses were performed on an ICP-OES, PerkinElmer Optima 3000XL with a detection limit of 1.4 μg l^{-1} for rhodium (1.4 ppb) and a determination limit of 4.2 μg l^{-1} for rhodium (4.2 ppb). All commercially available reagents were used without further purification, unless indicated otherwise. Silica alumina (silica-alumina catalyst support, grade 135) was purchased from Sigma Aldrich, $(SiO_2)_n$–CH_2CH_2COOH silica (SiliaBond®

Carboxylic Acid) was purchased from Silicycle Inc., γ-alumina (Merck KGaA, 70–230 mesh) was purchased from VWR International. Capping of silica alumina was performed as described earlier.[18]

Synthesis of 4,6-bis(diphenylphosphino)-10-(2-(pyridin-4-yl)-ethyl)-10H-phenoxazine (2). To a mixture of NixantPhos (10.3 g, 18.7 mmol) and tetrabutylammonium bromide (1.3 g, 3.9 mmol) in THF (100 mL) was added vinyl pyridine (20 mL, 185 mmol) and 10% NaOH solution (30 mL). The mixture was heated to gentle reflux for 24 hours. After cooling, the mixture was evaporated till dryness and water (500 mL) was added. The yellow solid was filtered off and washed 3 times with water (300 mL). The solid was dissolved in dichloromethane and subsequently washed with 200 mL water. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The remaining solid was recrystallized from a mixture of acetone (400 mL) and methanol (600 mL). Off-white 4,6-bis(diphenyl-phosphino)-10-(2-(pyridin-4-yl)ethyl)-10H-phenoxazine was collected (11.70 g, 96%).

^{1}H NMR (400 MHz): δ (ppm) 8.56 (d, ^3J = 6.0 Hz, 2H), 7.22 (m, 12H), 6.72 (pseudo-triplet, ^3J = 7.8 Hz), 6.52 (d, ^3J = 7.2 Hz, 2H), 6.05 (d, ^3J = 9.2 Hz, 2H), 3.8 (m, 2H), 3.0 (m, 2H).

^{13}C NMR (101 MHz): δ (ppm) 150.01 (C–H), 147.13 (C$_q$), 136.65 (t, ^1J(P,C) = 6.0 Hz, C$_q$), 133.68 (t, ^2J(P,C) = 11.1 Hz, C–H). 132.41 (C$_q$), 128.13 (C–H), 128.00 (C–H), 125.54 (C–H), 123.83 (C–H), 123.59 (C–H), 111.56 (C–H), 44.75 (CH$_2$), 30.48 (CH$_2$).

^{31}P NMR (162 MHz): δ (ppm) −19.02 (s).

FAB$^+$-MS: m/z calcd for $C_{43}H_{35}ON_2P_2$ ([MH]$^+$): 657.2225, obsd 657.2232.

Determination of adsorption constant and number of binding sites

For the determination of the adsorption constant and the number of binding sites, ten portions of silica were accurately weighed (ranging from 0–80 mg) and transferred to sealable vials. 2 mL portions of a 1.5 mM stock solution of **2** were added to each silica containing vial. The mixture was shaken at 21 °C for 17 hours. The equilibrated solutions were measured in a 1 mm light path cuvette. For optimum response 250 μL of the solution and 2000 μL of the corresponding solvent were added (9 times dilution). The cuvette was measured 3 times. After base-line correction the three measurements were averaged and analyzed. For the analysis the absorption at the absorption maximum 343 nm (ε = 9140 M^{-1} cm^{-1}) was determined and the results were plotted as [guest]$_{equilibrium}$ *versus* the amount of silica (in mg) and fitted to a (modified) Langmuir isotherm.[16]

Recycling experiments

A stainless steel HPLC column (25 cm × 4.6 mm ID × 1/4″ OD) was charged with 2.7 g methylated aluminosilicate, after which it was mounted in the reactor setup as depicted in Fig. 5. The lines, including the column, were washed with syngas saturated toluene prior to the hydroformylation experiments.

In a typical experiment, 1-octene (45 mL, 287 mmol) and THF (5 mL) were added to NixPy (39.3 mg, 0.06 mmol) and Rh-(acac)(CO)$_2$ (3.12 mg, 0.012 mmol) under an Ar atmosphere. At a temperature of 90 °C the reaction vessel was pressurized to 20 bars H$_2$/CO (1 : 1) by four purge cycles. After the desired time the reaction mixture was allowed to cool down to approximately 30 °C, at which temperature it was pumped out at 0.5 mL min^{-1}. During the entire procedure the system remained under 20 bars of syngas. When the reaction mixture was almost completely removed the flow direction was reversed and the column was flushed by 5 mL THF under 20 bars syngas at 0.15 mL min^{-1}. In the same way 45 mL 1-octene was transferred into the reaction vessel and the second run is initiated by heating the mixture to 90 °C. This entire procedure is repeated for the additional runs.

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