A Silica-Supported, Switchable, and Recyclable Hydroformylation−Hydrogenation Catalyst

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Abstract: A homogeneous hydroformylation catalyst, designed to produce selectively linear aldehydes, was covalently tethered to a polysilicate support. The immobilized transition-metal complex [Rh(**A**)CO]$^+$ (**1**$^+$), in which **A** is *N*-(3-trimethoxysilane-*n*-propyl)-4,5-bis(diphenylphosphino)phenoxazine, was prepared both via the sol−gel process and by covalent anchoring to silica. **1**$^+$ was characterized by means of ^{31}P and ^{29}Si MAS NMR, FT-IR, and X-ray photoelectron spectroscopy. Polysilicate immobilized Rh(**A**) performed as a selective hydroformylation catalyst showing an overall selectivity for the linear aldehyde of 94.6% (linear to branched aldehyde ratio of 65). In addition 1-nonanol, obtained via the hydrogenation of the corresponding aldehyde, was formed as an unexpected secondary product (3.6% at 20% conversion). Under standard hydroformylation conditions, **1**$^+$ and HRh(**A**)(CO)$_2$ (**1**) coexist on the support. This dual catalyst system performed as a hydroformylation/hydrogenation sequence catalyst (**Z**), giving selectively 1-nonanol from 1-octene; ultimately, 98% of 1-octene was converted to mainly 1-nonanal and 97% of the nonanal was hydrogenated to 1-nonanol. The addition of 1-propanol completely changes **Z** in a hydroformylation catalyst (**X**), which produces 1-nonanal with an overall selectivity of 93%, and completely suppresses the reduction reaction. If the atmosphere is changed from CO/H$_2$ to H$_2$ the catalyst system is switched to the hydrogenation mode (**Y**), which shows a clean and complete hydrogenation of 1-octene and 1-nonanal within 24 h. The immobilized catalyst can be recycled and the system can be switched reversibly between the three "catalyst modes" **X**, **Y**, and **Z**, completely retaining the catalyst performance in each mode.

Introduction

The development of well-defined catalyst systems that allow rapid and selective chemical transformations and at the same time can be completely recovered from the product is still a paramount challenge.[1] Although highly active and selective reusable catalyst systems have been reported, key problems for many systems comprise catalyst stability and leaching of catalytic material in the product phase.[2] An intensively studied and promising approach to facilitate catalyst−product separation is the attachment of homogeneous catalysts to polymeric organic, inorganic, or hybrid supports,[3,4] and more recently to dendrimeric[5,6] supports. Inorganic materials such as silica are particularly suited as heterogeneous catalyst supports because of their high physical strength and chemical inertness.

In the past three decades much research has been devoted to recyclable catalyst systems for the hydroformylation of higher alkenes. In the late seventies, alkoxysilane functionalized monophosphine ligands were used to tether a rhodium−phosphine complex to commercially available silica.[7] An interesting alternative for the preparation of silica-immobilized catalysts was presented by Panster et al., who used the sol−gel process,[8] i.e., a co-condensation of tetraalkoxysilanes and functionalized trialkoxysilanes.[9] The sol−gel technique is an ideal method for catalyst immobilization because of its diversity and its mildness.[10−13] The selectivity of the catalyst reported in

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(1) Baker, R. T.; Tumas, W. *Science* **1999**, *284*, 1477.

(2) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048.

(3) Extensive reviews on polymer immobilized catalysts include the following: (a) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189. (b) Hartley, F. R. *Supported Metal Complexes. A New Generation of Catalysts*; Reidel: Dordrecht, The Netherlands, 1985. (c) Iwasawa, Y. *Tailored Metal Catalysts*; Ugo, R., James, B. R., Eds.; Reidel: Dordrecht, The Netherlands, 1986. (d) Keim, W.; Driessen-Hölscher, B. *Handbook of heterogeneous catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinhein, Germany, 1997; Vol. 1, p 231.

(4) Alternative approaches toward catalyst−product separation include the following: (a) Aqueous biphasic catalysis: Cornils, B.; Herrmann, W. A. *Applied homogeneous catalysis with organometallic compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinhein, Germany, 1996; Chapter 3. (b) Supported aqueous phase catalysis: Arhanchet, J. P.; Davis, M. E.; Merola, J. S.; Hanson B. E. *Nature* **1989**, *339*, 454. (c) Fluorous phase catalysis: Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72. (d) Smart polymers: Bergbreiter, D. E.; Chandra, R. *J. Am. Chem. Soc.* **1987**, *109*, 174.

(5) For a review on this topic, see: Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1829.

(6) (a) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (b) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1526. (c) de Groot, D.; Eggeling, E. B.; de Wilde, J. C.; Kooijman, H.; van Haaren, R. J.; van der Made, A. W.; Spek, A. L.; Vogt, D.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, 1623. (d) Bourque, S. C.; Maltais, F.; Xiao, W.-J.; Tardiff, O.; Alper, H.; Arya, P.; Manzer, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 3035. (e) Bourque, S. C.; Alper, H.; Manzer, L. E.; Arya, P. *J. Am. Chem. Soc.* **2000**, *122*, 956.

(7) Farrell, M. O.; van Dyke, C. H.; Boucher, L. J.; Metlin, S. J. *J. Organomet. Chem.* **1979**, *172*, 367.

(8) Wieland, S.; Pantser, P. *Catal. Org. React.* **1994**, *62*, 383.

(9) Lindner, E.; Kemmler, M.; Mayer, H. A.; Weger, P. *J. Am. Chem. Soc.* **1994**, *116*, 348.

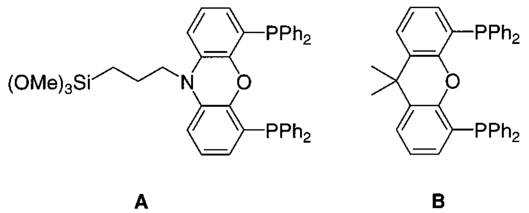
(10) Lindner, E.; Schneller, T.; Auer, F.; Mayer, H. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2154.

10.1021/ja010150p CCC: $20.00

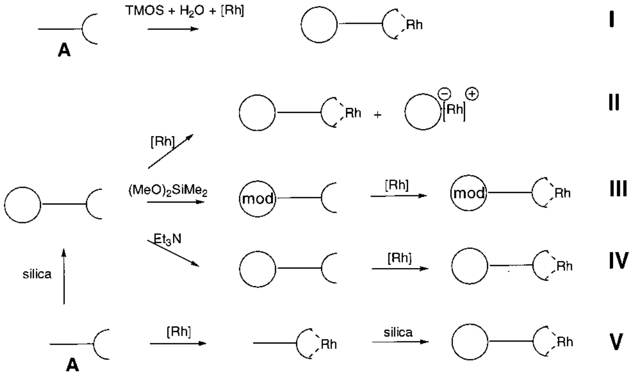
Pansters' work is rather low, but metal leaching was suppressed to a large extent. Blum et al. reported a sol−gel immobilized hydroformylation catalyst that is free of metal-leaching.[14] In the latter case no directing ligands were used which resulted in a lack of control over the product distribution. Immobilized hydroformylation catalysts that combine a high selectivity and activity with the absence of leaching of the catalytic material in the product phase have not been reported yet. For this purpose, catalysts containing monophosphines have proven not to be suitable thus far. A single ligand-to-metal bond appeared to be too weak and monophosphines generally give rise to a low selectivity. Diphosphines bind more strongly to rhodium than monophosphines due to the chelate effect.[15] Many rhodium diphosphine complexes give rise to a low selectivity in hydroformylation reactions, but Devon et al. described a diphosphine, BISBI, that showed a very high regioselectivity for the formation of linear aldehydes.[16] Casey et al. reported that rhodium diphosphine complexes with a large P−Rh−P (bite) angle can give rise to a high regioselectivity for the linear aldehyde.[17] We have designed a new generation of diphosphine ligands based on xanthene backbones that give extremely regioselective rhodium catalysts producing the linear aldehyde.[18,19]

The application of catalysts with large P−Rh−P bite angles in multiphase hydroformylation reactions appeared very successful as with these ligands a good catalyst performance was combined with a high ligand-to-metal bond strength. These properties resulted in selective two- and three-phase catalyst systems that were completely separated from the product phase and reused in numerous consecutive runs.[20] Preliminary results showed that under proper conditions a polysilicate immobilized rhodium complex, containing a xanthene-based diphosphine, gave rise to a very selective and sustainable hydroformylation process.[20b] Here we report a detailed study showing that the performance of such an immobilized catalyst is largely dependent on the conditions applied. Under standard conditions the system performed as a regioselective hydroformylation−hydrogenation cascade catalyst, which yielded a clean one-pot synthesis of 1-nonanol from 1-octene. Furthermore we will show that with small and simple manipulations, which affect the catalyst−support interactions, the system can be switched between three different catalyst modes. Depending on the conditions applied, the catalyst system can either function as a hydroformylation, a hydrogenation, or a hydroformylation/hydrogenation sequence catalyst. Moreover, upon recycling and reusing the system we can reversibly switch between these catalyst modes, thus using the same batch of catalyst for different types of reactions.

Chart 1



Scheme 1. Schematic Representation of Different Routes to Prepare Silica-Immobilized $[Rh(\mathbf{A})(CO)]^+$ ($\mathbf{1}^+$)



Results and Discussion

Catalyst Immobilization. The rhodium−diphosphine complex Rh(**A**) was immobilized on silica using the sol−gel technique and by a direct anchoring to commercially available silica. The latter method has been studied using different conditions. Both techniques are relatively straightforward procedures. Via the sol−gel process, Rh(**A**) was immobilized on a polysilicate support by stirring a solution of **A**, $[Rh(acac)(CO)_2]$, and tetramethyl orthosilicate (TMOS) in THF/H_2O to obtain $[Rh(\mathbf{A})CO]^+$ ($\mathbf{1}_{(\mathbf{I})}^+$) (Scheme 1-I).[20b] The resulting gel was dried and crushed into a free-flowing silica.

The immobilization of Rh(**A**) on commercially available silica was performed in four different ways to obtain $\mathbf{1}_{(\mathbf{II})}^+$ to $\mathbf{1}_{(\mathbf{V})}^+$ (Scheme 1-II to 1-V). In the first three approaches, **A** was covalently tethered to silica (to obtain silica(**A**)) by refluxing a suspension of **A** and silica in toluene for 2 h. The subsequent complexation of the rhodium precursor was performed under three different conditions. In the first approach the rhodium precursor $[Rh(acac)(CO)_2]$ and silica(**A**) were simply mixed together and stirred in a THF suspension (Scheme 1-II). In the second way, silica(**A**) was first reacted with dimethoxydimethylsilane to modify the acidic silanols on the silica surface.[24] To this end a suspension of silica(**A**) and dimethoxydimethylsilane was refluxed for 2 h in toluene and subsequently stirred in a solution of $[Rh(acac)(CO)_2]$ in THF at room temperature for

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[11] Lindner, E.; Schneller, T.; Auer, F.; Weger, P.; Mayer, H. A. *Chem. Eur. J.* **1997**, *3*, 1833.

[12] Schubert, U. *New J. Chem.* **1994**, *18*, 1049.

[13] Blum, J.; Avnir, D.; Schumann, H. *Chemtech* **1999**, 32.

[14] Blum, J.; Rosenfeld, A.; Polak, N.; Israelson, O.; Schumann, H.; Avnir, D. *J. Mol. Catal. A* **1996**, *107*, 217.

[15] Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1994.

[16] Devon, T. J.; Phillips, G. W.; Puckette, T. A.; Stavinoha, J. L.; Vanderbilt, J. J. U.S. Patent to Texas Eastman 4,694,109, 1987; *Chem. Abstr.* **1988**, *108*, 7890.

[17] Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavey, J. A.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

[18] Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081.

[19] van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.

[20] (a) Sandee, A. J.; Slagt, V. F.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, *17*, 1633. (b) Sandee, A. J.; van der Veen, L. A.; Reek, J. N. H.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3231. (c) Schreuder Goedheijt, M.; Hanson, B. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2000**, *220*, 1650. (d) Meehan, N. J.; Sandee, A. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Poliakoff, M. *Chem. Commun.* **2000**, 1497.

[21] Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethley, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 203.

[22] Bemi, L.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.

[23] Capka, M.; Czakoová, M.; Urbaniak, W.; Schubert, U. *J. Mol. Catal.* **1992**, *74*, 335.

[24] This method was reported to be equally efficient in the modification of silica surfaces as the use of chloroalkylsilanes: Sindorf, D. W.; Marciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767.

Table 1. Charactaristic Data of Immobilized [Rh(**A**)CO]$^+$ (**1**$_{(I)}$$^+$) Compared with Those of the Homogeneous Analogues[a]

	(**1**)$_{(I)}$$^+$	(**2**)$^+$(OTf)	(**2**)$^+$(BF$_4$)
^{31}P NMR	38 (br)[b]	36(br)[b]	
δ ppm (J_{P-Rh})		37.4 (d, 122 Hz)[c]	37.2 (d, 122 Hz)[c]
FT-IR	2011	2003	1998
ν(CO) (cm^{-1})			

[a] For more details see the Experimental Section. [b] Obtained by MAS solid-state NMR; J_{P-Rh} is too small for detection in the solid state.[c] Obtained by liquid-state NMR.

Table 2. Qualitative XPS Identification of the Elements Present in [Rh(**A**)CO]$^+$ Immobilized via the Sol−Gel Technique (**1**$_{(I)}$$^+$) Using [Rh(**B**)CO]$^+(BF)_4$ (**2**$^+$(BF$_4$)) as a Reference Compound and the Observed Binding Energies of the Specific Orbitals

	binding energies (eV)	
elements	[Rh(**A**)CO]$^+$ in sol−gel	[Rh(**B**)CO]$^+$(BF)$_4$
Si$_{2p}$	107.9	
P$_{2p}$	137[a]	134.1
B$_{1s}$		191.5
C$_{1s}$	289.3	287.1
Rh$_{3d}$	312.9	311.2
Rh$_{3d}$	317.4	315.1
N$_{1s}$	404.1	
O$_{1s}$	537.2	536.4
F$_{1s}$		687.1

[a] Very weak signal.

30 min (Scheme 1-III). In the third approach, [Rh(acac)(CO)$_2$] was added to a prestirred mixture of silica(**A**) and triethylamine in THF. The resulting suspension was stirred for 30 min at room temperature (Scheme 1-IV). For the last method the diphosphine rhodium complex was synthesized prior to the immobilization by adding [Rh(acac)(CO)$_2$] to a solution of **A** in THF and stirring the mixture for 30 min at room temperature. Predried silica was added to this reaction mixture and the suspension was stirred for 18 h (Scheme 1-V). All above-described catalyst systems were washed thoroughly and dried under reduced pressure before use.

Catalyst Characterization. System **1**$_{(I)}$$^+$ was characterized by means of solid-state ^{31}P MAS NMR and FT-IR, and the data were in good agreement with the fully characterized (homogeneous) cationic complexes **2**$^+$(OTf) and **2**$^+$(BF$_4$); **2**$^+$ = [Rh(**B**)CO]$^+$ (Table 1).[20b,25,26] **1**$_{(I)}$$^+$ showed a broad singlet at 38 ppm (versus a broad singlet at 36 ppm, observed for **2**$^+$(OTf)) in the ^{31}P MAS NMR spectrum. In the IR spectrum the carbonyl vibration was found at 2011 cm^{-1}, which is close to those found for **2**$^+$(OTf) (2003 cm^{-1}) and **2**$^+$(BF$_4$) (1998 cm^{-1}).

X-ray photoelectron spectroscopy (XPS) qualitatively identified the elements in **1**$_{(I)}$$^+$, and the characteristic electron binding energies compared well with those of **2**$^+$(BF$_4$) (Table 2).[27,28]

From XPS it was also determined that rhodium is only present in the oxidation state (I); no traces of metallic rhodium(0) were found in the samples.[29] The binding energies of the rhodium 3d electrons in **1**$_{(I)}$$^+$ were found to be 312 and 317 eV with a relative intensity of 3.3 and 2. This is comparable to the results of **2**$^+$(BF$_4$), for which binding energies of 311 and 316 eV with a relative intensity of 3.2 and 2 were found.[20b] These data are in good agreement with two-level-degenerated energy levels of the rhodium-3d electrons found for rhodium(I) compounds.[30]

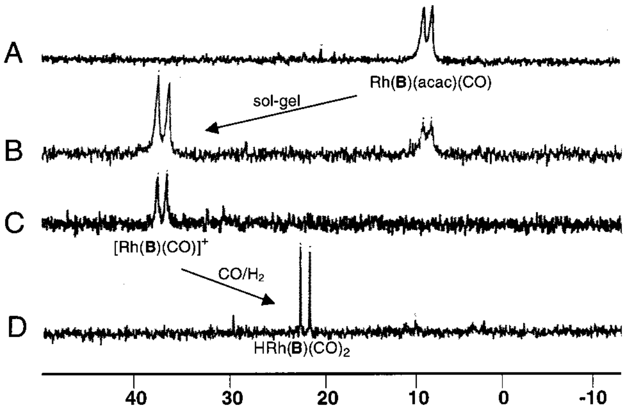

Figure 1. ^{31}P NMR spectra obtained during the sol−gel processing of [Rh(**B**)(acac)(CO)]: (A) [Rh(**B**)(acac)(CO)] in a soluble prepolymer mixture; (B) transformation from [Rh(**B**)(acac)(CO)] to [Rh(**B**)(CO)]$^+$; (C) transformation has been completed to [Rh(**B**)(CO)]$^+$ (the polymer has gelled at this stage); and (D) HRh(**B**)(CO)$_2$ in a wet polymer gel, obtained from [Rh(**B**)(CO)]$^+$ upon applying a CO/H$_2$ atmosphere.

The cationic complex formed during the sol−gel process, which was started by mixing **B** and [Rh(acac)(CO)$_2$] in a TMOS/H$_2$O/THF solution, was monitored using liquid-state ^{31}P NMR spectroscopy (Figure 1).[31] After [Rh(**B**)(acac)CO] was formed, as indicated by a broad doublet at 10 ppm and $J_{P,Rh}$ = 92 Hz, this complex quantitatively transformed into [Rh(**B**)CO]$^+$ (**2**$^+$) (doublet at 37 ppm; $J_{P,Rh}$ = 122 Hz) during the gelation process (Figure 1), having a siloxate as its counterion. Probably acidic silanols, formed during the hydrolysis of TMOS, protonate the acetylacetonate to acetylacetone. As a consequence **2**$^+$ is formed having a silicate counterion.[32] On exposing the gel containing **2**$^+$ to 1 bar of CO/H$_2$ (1:1) for 3 h at room temperature the color of the gel changed from orange to yellow. ^{31}P NMR studies elucidated the quantitative transformation of **2**$^+$ to [HRh(**B**)(CO)$_2$] (**2**) (doublet at 22 ppm; $J_{P,Rh}$ = 123 Hz), which is the key intermediate for a selective hydroformylation catalyst in a homogeneous phase (Figure 1).[18,19]

Since Si(OMe)$_4$ (Q elements) was used as the major silica precursor with only 5% of RSi(OMe)$_3$ (T elements) a dense silicate network was expected to be formed.[9] The presence of a rhodium complex in the sol−gel matrix can even give rise to a further increase in network density. The composition of the sol−gel manufactured silica was investigated by means of ^{29}Si MAS NMR (Figure 2). With this technique, the ratio of Si−O−Si versus Si−OH and Si−OR groups can be determined and the density of the network can be estimated from the ratio of silica atoms having a branching point of 4, 3, 2, or 1 (Q$_4$, Q$_3$, Q$_2$, and Q$_1$, respectively) by deconvoluting the relative peak areas.[10] For the silica material, prepared in the presence of **1**$_{(I)}$$^+$, we found a relative ratio of Q$_4$, Q$_3$, Q$_2$ of 49.0/40.5/10.2. (no terminal Q$_1$ was observed, and the amount of T elements was

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(25) It was observed that the stretch frequency of the carbonyl is influenced by the counterion of the complexes. The influence of the SiO$^-$ counterion of our immobilized complexes was found to be sensitive to the presence of traces of a protic solvent.

(26) van der Veen, L. A.; Keeven, P. H.; Schoemaker, G. C.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 872.

(27) Tang, L.; Huang, M.; Liang, Y. *Chin. J. Polym. Sci.* **1996**, *14*, 199.

(28) Valuable information on transition metal complexes on a silica support was recently obtained using EXAFS: Bianchini, C.; Burnaby, D. G.; Evans, J.; Frediani, P.; Meli, A.; Oberhauser, W.; Psaro, R.; Sordelli, L.; Vizza, F. *J. Am. Chem. Soc.* **1999**, *121*, 5961.

(29) Besson, M.; Gazelot, P.; Pinel, C.; Neto, S. *Heterog. Catal. Fine Chem. IV* **1997**, 215.

(30) Niemantsverdriet, J. W. *Spectroscopy in Catalysis*; Weinheim, Germany, 1995.

(31) Nonimmobilized complexes can be studied easily during the sol−gel process by means of liquid-state NMR. This is not possible for the immobilized rhodium siloxantphos complex (Rh(A)).

(32) Ion pairs of cationic rhodium−phosphine species on silica were previously observed by Basset et al. via the protonation of rhodium−allyl groups by the silica: Scott, S. L.; Dufour, P.; Santini, C. C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2011.

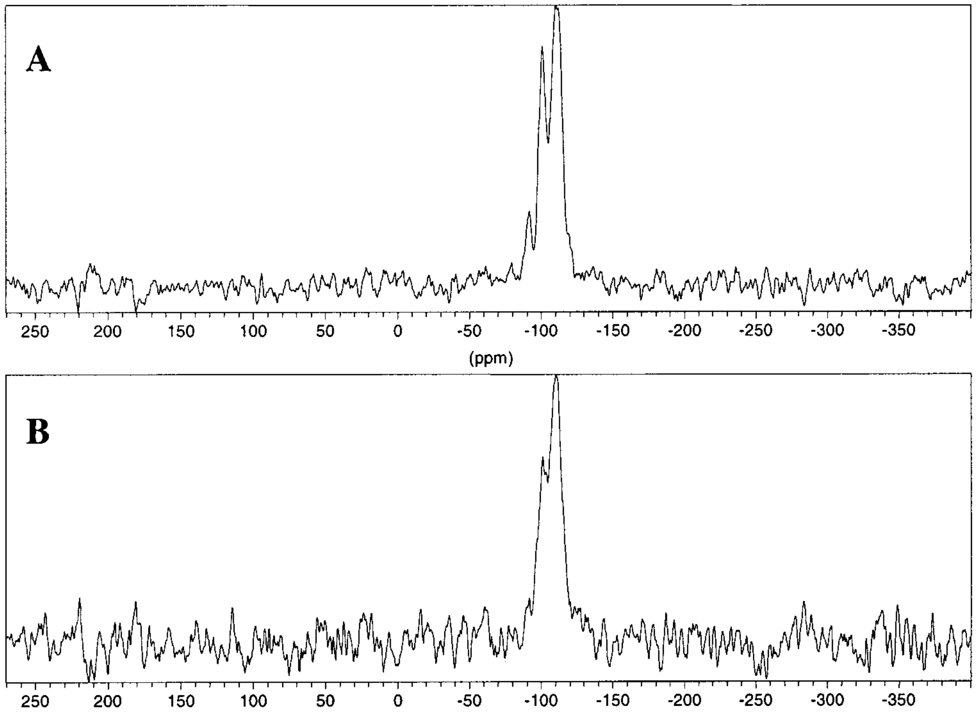

Figure 2. ^{29}Si MAS NMR spectra of the Si-support of the sol−gel immobilized [Rh(**A**)(CO)]$^{+}$ ($\mathbf{1}_{(I)}^{+}$) (A) and [Rh(**B**)(CO)]$^{+}$ ($\mathbf{2}^{+}$) (B).

Table 3. Hydroformylation of 1-Octene Using Polysilicate-Immobilized [Rh(**A**)CO]$^{+}$ ($\mathbf{1}_{(I)}^{+}$)[a]

entry/ (method of preparation)	time (h)	conversion (%)	TOF[b] (h^{-1})	l/*b* ratio	l-aldehyde (%)	b-aldehyde (%)	l-alcohol (%)	octene isomers/ octane (%)
1/(I)	2	20	18.3	65	94.6	1.5	3.6	0.2
2/(II)	0.5	97	n.d.	2	40.1	22.0	0	37.9
3/(III)	23	24	8.0	19	85.5	4.5	0	9.9
4/(IV)	22	18	8.7	37	96.2	2.6	1.0	0.2
5/(V)	22	37	13.2	37	90.7	2.6	5.1	1.6
6/(homog.)	2	19	283	32	93.3	2.9	0	3.7
7/(no ligand)	2	72	119	2	70.0	28.9	0.1	1.0

[a] $P(CO/H_2)$ (1:1) = 50 bar, temperature = 80 °C, ligand:Rh = 10, substrate:Rh = 637:1, Rh content 10 μmol. Samples were analyzed by means of GC and GC-MS analysis. [b] Average turnover frequencies were calculated as (mol product)(mol catalyst)$^{-1}$h^{-1}, n.d. = not determined.

too low to detect, Figure 2A). For the silica material, prepared in the presence of $\mathbf{2}^{+}$, comparable results were obtained; a Q_4, Q_3, Q_2 ratio of 57.5/37.5/4.9 was observed (Figure 2B).[34] These results indicate that the network density of these systems is indeed very high and the copolymerization of 5% of $RSi(OMe)_3$ (**A**) yields only slightly less dense networks.

The Impact of the Catalyst Preparation Procedure on Catalysis. The method of catalyst immobilization appeared to affect its performance in catalysis. When the catalyst was synthesized via route II the catalyst showed a low selectivity in the hydroformylation of 1-octene (the linear to branched aldehyde ratio was even lower than 2) (Table 3, entry 2), whereas the route V catalyst is highly selective toward the linear aldehyde (with a linear-to-branched ratio of 37) (Table 3, entry 5). In accordance with examples from literature it is likely that the former preparation procedure gives rise to the ionic bonding of ligand-free rhodium cations on the slightly acidic silica surface.[22,35] If the rhodium phosphine complex is prepared prior to anchoring (route V) no ligand-free rhodium is attached to the silica. We also succeeded in eliminating the disturbing effect of the acidic silanols on the catalyst preparation via the chemical modification of the silica surface (route III) or upon addition of a neutralizing base (route IV). Premodification of the silica using dimethoxydimethylsilane (III) largely improved the catalyst selectivity (linear to branched aldehyde ratio of 19, Table 3, entry 3) at the cost of some activity.[22] The addition of triethylamine (IV) also resulted in a very good hydroformylation catalyst (with a linear to branched aldehyde ratio of 37, Table 3, entry 4).

System $\mathbf{1}_{(I)}^{+}$, immobilized via the sol−gel process (Scheme 1-I), performed very well in the hydroformylation of 1-octene. The selectivity for the linear aldehyde of $\mathbf{1}_{(I)}^{+}$ was found to be as high as 94.6%, which equals that of its homogeneous analogue (Table 3, entries 1 and 6). Again, the preformation of the rhodium diphosphine complex before immobilization avoided the formation of ligand free rhodium cations on the silica surface. This approach gives rise to a well-defined, very selective hydroformylation catalyst.

The high network density of immobilized $\mathbf{1}_{(I)}^{+}$, obtained via the sol−gel process, was expected to have implications on the catalysis; it can result in a good recyclability due to its rigidity, but at the same time it might decrease the catalyst activity due to the blocking of catalyst sites.[9] The sol−gel immobilized

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[33] A transition metal can serve as an extra junction in the silica network and it can also catalyze the polycondensation process. This was previously observed by Lambert and Gonzalez: Lambert, C. K.; Gonzalez, R. D. *Microporous Mater.* **1997**, 179.

[34] The resolution of Figure 2A is better than that of Figure 2B due to a difference in the number of scans.

[35] Yao, J.-Z.; Chen, Y.-Y.; Tian, B.-S. *J. Organomet. Chem.* **1997**, *534*, 51.

Table 4. Hydroformylation of 1-Octene Using Sol−Gel and Silica-Immobilized Catalyst [Rh(**A**)CO]$^+$ (**1**$^+$) in Subsequent Catalytic Runs[a]

entry [cycle]	meth of prep.	time (h)	conversion (%)	TOF[b] (h^{-1})	l/b ratio	l-aldehyde (%)	b-aldehyde (%)	l-alcohol (%)	octene isomers/ octane (%)
1 [1]	I	2	20	18	65	94.6	1.5	3.6	0.2
2 [2]	I	2	19	26	43	90.0	2.2	5.1	2.6
3 [3]	I	2	19	25	35	87.6	2.7	6.7	3.0
4 [4]	I	2	12	12	62	89.6	1.6	8.8	0
5 [1]	I	18	38	23	22	61.0	4.1	29.6	5.3
6 [2]	I	18	30	17	25	77.9	3.7	15.1	3.4
7 [1]	V	22	37	13	37	90.7	2.6	5.1	1.6
8 [2]	V	22	41	15	45	91.5	2.1	4.0	2.4
9 [3]	V	72	61	8	27	79.9	3.5	13.2	3.4
10 [1]	III	23	24	8	19	85.5	4.5	0	9.9
11 [2]	III	23	23	8	20	87.3	4.5	0	8.3
12 [3]	III	23	22	8	16	83.7	5.2	0	11.1
13[4]	III	72	44	5	16	84.8	5.4	0	9.8
14 [1]	I[c]	24	69	35[d]	32	92.8	3.0	2.5	1.7
15 [2]	I[c]	24	69	36[d]	36	94.1	2.7	1.2	2.0
16 [3]	I[c]	24	69	36[d]	35	94.0	2.7	1.0	2.3
17 [4]	I[c]	24	67	35[d]	35	94.5	2.7	1.3	2.2
18(silica/Et$_3$N)	I[e]	2.5	7	4	33	92.0	2.8	0	5.2

[a] P(CO/H$_2$) (1:1) = 50 bar, temperature = 80 °C, ligand:Rh = 10, substrate:Rh = 637:1, Rh content 10 μmol. Samples were analyzed by means of GC and GC-MS analysis. [b] Average turnover frequencies were calculated as (mol product)(mol catalyst)$^{-1}$ h^{-1}. [c] 1 mL of 1-propanol added to the catalyst mixture. [d] Initial turnover frequency. [e] 1 mL of triethylamine added to the catalyst mixture.

catalyst, however, was slightly faster than the silica immobilized analogue (Table 3, entries **1** and **5**), indicating that the catalytic sites are fully accessible.[12]

Influence of the Silica on the Catalyst Recycling Properties. Sol−gel and silica immobilized Rh(**A**) were tested in successive hydroformylations of 1-octene to investigate the effect of the support on the recyclability of the catalyst (Table 4, entries 1−6 and 7−9, respectively). For both systems the ratio of linear aldehyde, branched aldehyde, and octene isomers was found to be comparable with the homogeneous analogue (Table 3, entry 6). Upon recycling, the high regioselectivity for the linear aldehyde was maintained (linear-to-branched ratios ranging from 22 to 65) while only a few percent of alkene isomers was formed as a side product (ranging from 0 to 3.4%). Interestingly, we observed a small decrease in hydroformylation activity upon recycling along with an increasing formation of 1-nonanol (4−9%), an effect that becomes more pronounced (up to 30%) at longer reaction times (Table 4, entries 5 and 6). We have not observed this phenomenon in analogous homogeneous hydroformylation reactions, suggesting that the silica support plays a key role in this secondary reaction. We suggest that the acidic silica increasingly blocks the formation of HRh(**A**)(CO)$_2$ **1**$_{\mathbf{(I)}}$ from **1**$_{\mathbf{(I)}}^+$ (vide infra), resulting in an increase in hydrogenation activity[39] and a small decrease in hydroformylation activity.[36,37]

When the silica material with the capped (acidic) silanols was used (Scheme 1-III), the influence of the silica on the recyclability of the hydroformylation catalyst was largely suppressed. No hydrogenation of the aldehyde was observed as a secondary reaction in any of the successive catalytic runs (Table 4, entries 10−13). The modification of the surface silanols with alkylsilanes did not yield an optimal catalyst system. The overall selectivity for the linear aldehyde (ranging from 83.7 to 87.3%) was slightly lower compared with the other catalysts; more isomerization (8.3 to 11.1%) and branched aldehyde (4.5 to 5.4%) was obtained. As yet we do not have a plausible explanation for this.

Interestingly, we found a more subtle method to reduce the influence of the silica. In the presence of 1 mL of 1-propanol, which is approximately 7% of the total volume of the reaction mixture, an efficient suppression of hydrogenation activity has been realized; a high overall selectivity for the linear aldehyde (ranging from 92.8 to 94.5%) was obtained in subsequent batchwise runs (Table 4, entries 14−17). The effect of the presence of 1-propanol is in contrast with previously reported examples of hydroformylation catalysts, to which alcohols or amines were added to *promote* the hydrogenation of aldehydes via a transfer hydrogenation reaction.[38] In the present case the alcohol prevents the formation of the hydrogenation catalyst from the hydroformylation catalyst by deactivating the acidic silanols on the silica surface. The addition of triethylamine as a base also enabled the suppression of the hydrogenation activity (Table 4, entry 18).

It is evident that the silica support influences the catalytic performance and in the following part we describe experiments that provide a better insight into the processes involved. In the sol−gel state the immobilized cationic complex **1**$_{\mathbf{(I)}}^+$ completely transforms to the rhodium hydride species **1**$_{\mathbf{(I)}}$ under a CO/H$_2$ atmosphere (Figure 1) (vide supra). On dried silica, however, this conversion might not be complete since the dried support is more acidic.[40] Hence, **1**$_{\mathbf{(I)}}^+$ and **1**$_{\mathbf{(I)}}$ probably coexist on the silica support. To investigate the effect of dried silica on these types of complexes, several experiments in solution were performed using Rh(**B**).

Upon the addition of predried silica to a yellow solution of **2** in toluene, the solution slowly decolorized and the silica turned

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(36) *Rhodium Catalyzed Hydroformylation*; van Leeuwen, P. W. N. M., Claver, C., Eds.; Kluwer Acedemic Publishers: Dordrecht, The Netherlands, 2000.

(37) *Homogeneous Hydrogenation*; Chaloner, P. A., Esteruelas, M. A., Joó, F., Oro, L. A., Eds.; Kluwer Acedemic Publishers: Dordrecht, The Netherlands, 1994.

(38) (a) Kaneda, K.; Imanaka, T.; Teranishi, S. *Chem. Lett.* **1983**, 1465. (b) Anderson, J.-A.; Currie, A. W. S. *Chem. Commun.* **1996**, 1543.

(39) Although rhodium-catalyzed hydrogenation of carbonyl groups is not a commonly used synthetic route for the production of alcohols, the mechanism of this reaction is well understood. See (besides ref 36) for example: Törös, S.; Lollár, L.; Heil, B.; Markó, L. *J. Organomet. Chem.* **1983**, *255*, 377.

(40) The decrease in the capacity of silica to form hydrogen bridges on drying gives rise to an increase in acidic sites on the silica surface. The addition of a protic solvent (water or alcohol) to dried silica will facilitate hydrogen bond formation and thereby neutralize the acidity: van Roosmalen, A. J.; Mol, J. C. *J. Phys. Chem.* **1979**, *83*, 2485.

Table 5. Hydroformylation (**X**) and Hydrogenation (**Y**) Activities of $[Rh(\mathbf{B})(CO)]^+(CF_3COO)^-$ ($\mathbf{2}^+$) and $HRh(\mathbf{B})(CO)_2$ (**2**)[a]

catalyst (reaction)	time (h)	conversion (%)	TOF[b] (h^{-1})	L/b ratio	l-aldehyde (%)	b-aldehyde (%)	l-alcohol (%)	octane/octene isomers[c] (%)
$\mathbf{2}^+$ (**X**)	2	12	21	>50	75.3	0	0	24.7[d]
$\mathbf{2}'^{e}$ (**X**)		20	187	52	94.5	1.8	0	3.7
$\mathbf{2}^+$ (**Y**)	2	16	22				100	
2 (**Y**)	2	0	0				0	

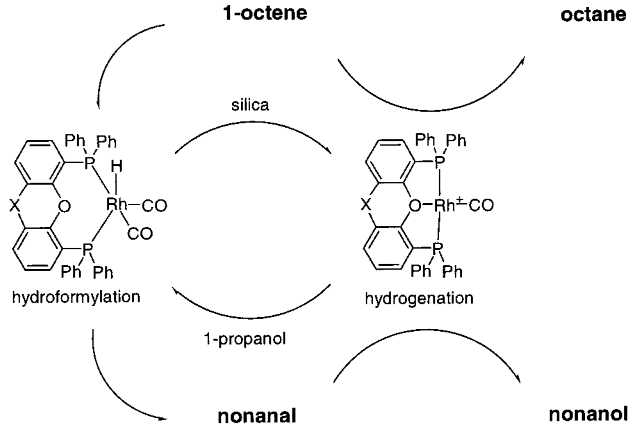
[a] Temperature = 80 °C, ligand:Rh = 10, Rh content 10 μmol, substrate:Rh = 637:1, using 1 mL of 1-octene (in case of **X**) and 1 mL of 1-nonanal (in case of **Y**) as the substrate, $P(CO/H_2)$ (1:1) = 50 bar (in case of **X**) and $P(H_2)$ = 50 bar (in case of **Y**), unless else stated. Samples were analyzed by means of GC and GC-MS analysis. [b] Average turnover frequencies were calculated as (mol product)(mol catalyst)$^{-1}$ h^{-1}. [c] Octane and alkene isomers are not quantitatively separable on GC. [d] Of which approximately 50% was octane. [e] Data taken from ref 19, reaction performed under 20 bar of CO/H_2 and 80 °C at a ligand-to-metal ratio of 5.

orange. This silica "adsorbed" rhodium diphosphine complex indeed appeared to be the cationic species $\mathbf{2}^+$ as indicated by the carbonyl vibration at 1972 cm^{-1} in the IR spectrum.[25] The rhodium−hydrido complex **2** is converted to $\mathbf{2}^+$ by the silica, probably via a protonation of the rhodium hydride, which after elimination of H_2 yields the cationic species.[41] Upon the addition of 20 μL of trifluoroacetic acid to a mixture of **2** in d_6-benzene a similar protonation resulted in the formation of $\mathbf{2}^+(CF_3COO^-)$, as indicated by ^{31}P NMR that showed a broad doublet at 38 ppm; $J_{P,Rh} = 111$ Hz.[42] This supports the idea that the conversion of **2** to $\mathbf{2}^+$ indeed occurs via a simple protonation.

The catalytic performance of $\mathbf{2}^+$ is significantly different from that of the rhodium hydride analogue, **2**. The activity of $\mathbf{2}^+(CF_3COO^-)$ in the hydroformylation of 1-octene was investigated by monitoring a mixture of **2**, CF_3COOH, and 1-octene in toluene under standard hydroformylation conditions (Table 5, entry 1). After 2 h, 12% of 1-octene was converted; 75% of the products were aldehydes (TOF = 21 mol·mol^{-1}·h^{-1}) while the remaining 25% was octane, obtained by hydrogenation of 1-octene. Compared to **2** (Table 5, entry 2), the hydroformylation rate of $\mathbf{2}^+$ was a factor 10 lower, but the hydrogenation activity was significantly higher.[39]

Generally, the catalyst for hydroformylation is a neutral rhodium(I) hydride species[36] that is clearly distinct from the species that are active for hydrogenation.[37] The hydrogenation catalysts are cationic Rh(I)$^+$ or neutral Rh(I)Cl species. Often rhodium(I) salts are used as the precursor for hydroformylation catalysts. Although there are several papers that seem to invoke cationic species as the catalysts, under the reaction conditions (H_2, CO, temperature > 25 °C) these salts are converted to a rhodium hydride complex.[43] Anions that have been used include halides, conjugate bases of weak acids, thiolates, alkoxides, etc. The frequently reported "promoting" effect of bases such as amines is based on more efficient formation of the active rhodium hydride by neutralizing the formed strong acids (HI, HCl, HBr, HBF_4). Rhodium salts of weaker acids, like thiolates, are smoothly converted into the rhodium hydride without the addition of base.[44−46] Stanley reported hydroformylation catalysts that differ from the rhodium hydride species consisting of bimetallic rhodium complexes.[47]

Scheme 2. Representation of the Interconversion of the Catalyst Systems $[Rh(\mathbf{A})(CO)]^+$ ($\mathbf{1}^+$) and $[HRh(\mathbf{A})(CO)_2]$ (**1**) and the Products Generated from Each Catalyst Species



The hydrogenation activity of both $\mathbf{2}^+(CF_3COO^-)$ and **2** was further compared in the hydrogenation of 1-nonanal under 50 bar of H_2. Catalyst $\mathbf{2}^+(CF_3COO^-)$ showed a significant hydrogenation of the aldehyde to the corresponding alcohol (16% conversion within 2 h reaction time, Table 5, entry 3), whereas the rhodium hydride complex **2** is completely inactive in this reaction (Table 5, entry 4). The presence of both complexes on the silica support thus explains the observed cascade of a hydroformylation followed by a hydrogenation reaction. These experiments support the proposal that in the silica-immobilized system $\mathbf{1}^+$ and **1** coexist on the polysilicate surface and that $\mathbf{1}^+$ must be formed from **1** by a protonation of the rhodium-hydride by the silica support since this is the only acid present in the reaction mixture.

The neutralizing effect of alcohols on the silica-supported cationic rhodium species was illustrated by the addition of 1-propanol (under 1 atm of CO/H_2) to a suspension of silica "adsorbed" $\mathbf{2}^+$ in toluene. This resulted in a decolorization of the silica while the toluene turned yellow; Rh(**B**) was "desorbed" from the silica under formation of the rhodium hydride **2** as indicated by the appearance of a doublet at 21 ppm; $J_{Rh,P}$ = 125 Hz in the ^{31}P NMR spectrum (Scheme 2). The presence of alcohol sufficiently decreases the acidity of the silica, which becomes unable to protonate the rhodium hydride species.[40] Hence $\mathbf{2}^+$ is completely transformed to the rhodium hydride **2** under a CO/H_2 atmosphere in the presence of alcohol.[42] Consequently, the catalytic performance using Rh(**A**), immobilized on polysilicates, can be controlled by the addition of small amounts of alcohol.

Hydroformylation−Hydrogenation Cascade Reaction. Under standard hydroformylation conditions, the cationic species

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(41) The bonding of a rhodium phosphine carbonyl complex to a silica surface was previously applied via the protonation of a rhodium−methyl bond: Scott, S. L.; Szpakowicz, M.; Mills, A.; Santini, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 1883.

(42) The reversible protonation and hydrogenation of a comparable rhodium hydride viz. $HRh(CO)(TPPTS)_3$ was previously observed: Herrmann, W. A.; Kulpe, J. A. *J. Organomet. Chem.* **1990**, *389*, 85.

(43) Kwok, T. J.; Wink, D. J. *Organometallics* **1993**, *12*, 1954.

(44) Park, H. S.; Alberico, E.; Alper, H. *J. Am. Chem. Soc.* **1999**, *121*, 11697.

(45) Diégues, M.; Claver, C.; Masdeu-Bultó A. M.; Ruiz, A.; van Leeuwen, P. W. N. M.; Schoemaker, G. C. *Organometallics* **1999**, *18*, 2107.

(46) Pàmies, O.; Net, G.; Ruiz, A.; Bo, C.; Poblet, J. M.; Claver, C. *J. Organomet. Chem.* **1999**, *586*, 125.

(47) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W. J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784.

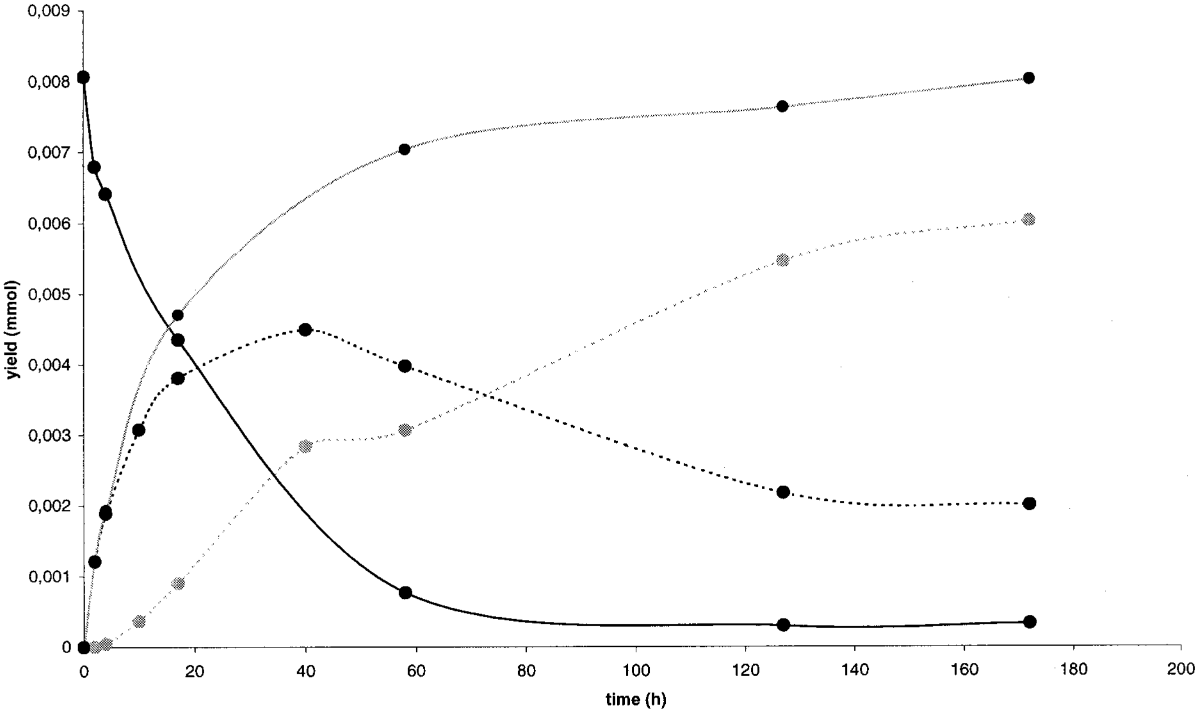

Figure 3. Course of the hydroformylation−hydrogenation sequence reaction of 1-octene using sol−gel immobilized Rh(**A**). The black line represents the 1-octene concentration, the black dotted line 1-nonanal, the gray line the sum of 1-nonanal and 1-nonanol, and the gray dotted line 1-nonanol. For detailed information about the conditions applied, see the Experimental Section.

1^+ and the hydridic complex **1** coexist on the support. Hence hydroformylation and hydrogenation will both proceed under a CO/H_2 atmosphere. Via a hydroformylation−hydrogenation of 1-octene using Rh(**A**), immobilized via the sol−gel process (Scheme 1-I), we performed a clean one-pot reaction of 1-octene to 1-nonanol. 98% of the 1-octene was converted in the hydroformylation reaction and 97% of the linear nonanal was subsequently hydrogenated to 1-nonanol resulting in an overall selectivity of 90% for the linear alcohol after 328 h.[48] Since both reactions are rate dependent in substrate, the overall reactivity of the cascade reaction is low. For commercial purposes, the reactivity of the current system, applied as a cascade reactor, is too slow as yet. Importantly, no heavy-end side products were observed in this reaction owing to the mild conditions applied.

On monitoring such a cascade reaction, mainly the hydroformylation of 1-octene to the aldehyde was observed in the first few hours (Figure 3). The hydrogenation toward the corresponding alcohol started at higher aldehyde concentrations. When approximately 90% of the 1-octene was consumed (at 60 h) the hydroformylation activity had decreased significantly, which is in line with the first-order rate dependency in substrate. In contrast, the hydrogenation of the aldehyde product proceeded. As a result, the aldehyde concentration decreased again after approximately 40 h, which in turn caused a decrease of the hydrogenation rate. After 175 h the hydroformylation of 1-octene has proceeded up to 97% and the subsequent aldehyde hydrogenation up to 75% conversion.[49]

Such a clean, one-pot hydroformylation−hydrogenation cascade system,[50] producing a high yield of the linear product with a high regioselectivity, is uncommon for rhodium catalysts.[51] Moreover, we can control the ratio of the two coexisting catalyst species 1^+ and **1** and we are able to recycle the catalyst completely as a result of the heterogeneous nature of the system. The combination of these properties can be utilized for a multipurpose system that can be switched between a pure hydroformylation catalyst (**X**), a pure hydrogenation catalyst (**Y**), and a hydroformylation−hydrogenation (**Z**) sequence catalyst (Scheme 3).

Modulation of the Catalyst Functionality. We started a series of catalyst experiments on 1-octene, using polysilicate immobilized Rh(**A**), with a reaction under standard conditions, thus with the catalyst system in the **Z** mode. The reaction was stopped after 172 h, which resulted in a product mixture that consisted of 66.7% of 1-nonanol and 18.5% of 1-nonanal (Table 6, entry 1). After this reaction we recycled the system and transformed it into a hydrogenation catalyst (**Y**) just by washing it with toluene and subsequently adding a mixture of 1-octene and 1-nonanal in toluene to the catalyst mixture. After a reaction time of 24 h under an H_2-atmosphere a complete hydrogenation of both substrates was observed to octane and 1-nonanol, respectively (Table 6, entry 2). This shows that the switch from the **Z** to the **Y** mode was accomplished by simply replacing

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(48) This result was obtained using a reaction mixture of 14 mL of toluene, 0.5 mL of 1-octene, and 0.5 mL of decane. The obtained exact product distribution was the following: 1-nonanol (89.8%), octane (4.5%), l-nonanal (2.3%), b-nonanal (0.7%), and b-alcohol (0.7%).

(49) The decreased hydrogenation activity at higher conversions is most probably caused by the increased alcohol concentration; the silica becomes less acidic and the hydrogenation catalyst 1^+ transforms to **1**. Full conversion to the alcohol is obtained at lower substrate concentration, see ref 48.

(50) For a review on tandem reaction sequences under hydroformylation conditions see: Eilbracht, P.; Bärfacker, L.; Buss, C.; Hollmann, C.; Kitsos-Rzychon, B. E.; Kranemann, C. L.; Rische, T.; Roggenbuck, R.; Schmidt, A. *Chem. Rev.* **1999**, *99*, 3329.

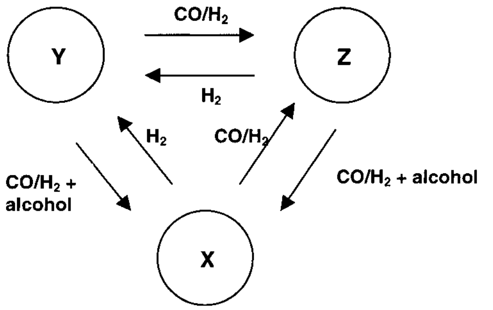
(51) Examples of rhodium-catalyzed hydrocarbonylation include the following: (a) Johnson, P.; Lawrenson, M. J. Fr. Dem. 1.549.414, 1968; *Chem. Abstr.* **1970**, *72*, 2995. (b) Lawrenson, M. J. UK Patent 1.284.615, 1972; *Chem. Abstr.* **1972**, *77*, 125 982. (c) Lawrenson, M. J. UK Patent 1.254.222, 1971; *Chem Abstr.* **1972**, *76*, 33 787. (d) Fell, B.; Barl, M. *J. Mol. Catal.* **1977**, *2*, 301. (e) Zhou, J.-Q.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1991**, 233. (f) MacDougall, J. K.; Simpson, M. C.; Green, M. J.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1161. (g) Anderson, J.-A. M.; Currie, A. W. S. *Chem. Commun.* **1996**, 1543. The cobalt−phosphine based Shell hydroformylation process produces alcohols with linearities up to 80% in a similar reaction sequence: Arnoldy, P. *Rhodium catalyzed hydroformylation*; van Leeuwen, P. W. N. M., Claver C., Eds.; Kluwer Acedemic Publishers: Dordrecht, The Netherlands, 2000; p 203.

Table 6. Results from Switching between Hydrogenation (**Y**), Hydroformylation (**X**), and Hydroformylation−Hydrogenation Sequence (**Z**) Reactions Using Sol−Gel Immobilized $[Rh(\mathbf{A})CO]^+$ ($\mathbf{1}_{(I)}{}^+$)[a]

entry/ (reaction)	time (h)	conversion octene (%)	conversion aldehyde (%)	l/b	l-aldehyde (%)	b-aldehyde (%)	l-alcohol (%)	octane[b] (%)
1/(**Z**)	172	97	75	23	18.5	3.6	66.7	11.2
2/(**Y**)	24	100	100		0	0	100	100
3/(**Z**)	68	60	16	18	65.2	4.5	13.7	16.6
4/(**Y**)	2	98	10		0	0	9.7	98
5/(**X**)	96	96	0	18	90.7	5.1	0	4.3

[a] Temperature = 80 °C, ligand:Rh = 10, Rh content 10 μmol, substrate:Rh = 637:1, using 1 mL of 1-octene (**X** and **Z**) (plus 1 mL of 1-nonanal in the case of **Y**) as the substrate(s), $P(CO/H_2)$ (1:1) = 50 bar (**X** and **Z**) or $P(H_2)$ = 50 bar (**Y**). Samples were analyzed by means of GC and GC-MS analysis. [b] Numbers include isomers of 1-octene since these are not separable from octane on GC.

Scheme 3. Control over Catalyst Function by Changing the Reaction Conditions[a]



[a] **X** = hydroformylation, **Y** = hydrogenation and **Z** = hydroformylation/hydrogenation sequence.

the CO/H_2 for an H_2 atmosphere. More importantly, we observed that this modulation is reversible; in the third catalyst cycle the system was applied again as a **Z**-sequence catalyst by changing the atmosphere from H_2 to CO/H_2 and using 1-octene as the substrate. This resulted in a switch of the catalyst from the hydrogenation mode back to the hydroformylation−hydrogenation sequence mode. The regioselectivity for the linear aldehyde and alcohol (overall linear-to-branched ratio of 18) was largely restored (Table 6, entry 3). This indicates that the catalyst did not decompose upon switching between these two modes, since even a few percent of decomposed rhodium catalyst would generally result in a dramatic drop in regioselectivity.

In the fourth cycle, once more the system was switched back from the **Z** to the **Y** mode (Table 6, entry 4). This time, the hydrogenation reaction of a 1:1 mixture of 1-octene and 1-nonanal was stopped after 2 h and a chemoselectivity for the alkene reduction over aldehyde reduction was observed (96% alkene and 10% aldehyde was hydrogenated).[52] From these four catalytic runs it can be concluded that the immobilized catalyst system is switched easily and repeatedly between the hydrogenation mode and the hydroformylation−hydrogenation cascade mode. We subsequently investigated, in the fifth run, the switch of the system to a pure hydroformylation catalyst (Table 6, entry 5). The atmosphere was changed from H_2 to CO/H_2 and 1 mL of 1-propanol was added to the catalyst along with a fresh batch of 1-octene in toluene. After 96 h 1-octene was almost completely converted to the linear aldehyde with a complete suppression of its hydrogenation to the alcohol! Hence, the catalyst modulation between all three catalyst functionalities was successfully accomplished upon small changes of the reaction conditions.

Conclusion

We have developed a polysilicate immobilized homogeneous catalyst system that can act both as a hydrogenation and a regioselective hydroformylation catalyst. This system has been used for a clean one-pot synthesis of 1-nonanol from 1-octene via a hydroformylation−hydrogenation cascade reaction and could be quantitatively recovered from the product. The catalyst−support interactions were fully controlled and easily manipulated by simple changes in the reaction conditions. This enabled a reversible switching of the catalyst mode between a hydroformylation, a hydrogenation, and a hydroformylation/hydrogenation cascade catalyst. In view of the increasing demand for greener chemical processes the current system exhibits several important properties: (1) it affords a quantitative and straightforward separation of the catalyst from the products, (2) it is reusable in numerous catalytic cycles without any deterioration of the catalytic activity,[20d] and (3) it enables clean and selective reactions for different important catalytic processes using only one catalyst system.

Experimental Section

Materials. 4,5-Bis(diphenylphosphino)phenoxazine[19] and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene[18] were synthesized according to literature procedures. 1-Octene was purified over neutral alumina prior to its use. All other chemicals were purchased commercially and used without further purification. Solvents were dried prior to their use. Hexane, pentane, diethyl ether, THF, toluene, and benzene were distilled from sodium. Dichloromethane and triethylamine were distilled from calcium hydride. All solutions and solvents not stated above were degassed under argon prior to their use. All reactions were performed under Schlenk conditions using Argon as the inert atmosphere.

Analytical Techniques. NMR spectra were recorded on a Bruker AMX 300 or DRX 300 spectrometer. Chemical shifts are in ppm relative to TMS as external standard unless otherwise stated. Solid-state ^{31}P MAS NMR chemical shifts are relative to $NH_4H_2PO_4$ (at 0.8 ppm) and ^{29}Si MAS NMR chemical shifts are relative to Zeolite A (at −89 ppm) and Q_8M_8 (at 11.85 ppm). The correct pulse delays were determined at 20 s for the ^{31}P MAS NMR and 5 min for the ^{29}Si MAS NMR at a spinning rate of 10.000−11.000 Hz. FT-IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer. Mass spectra (FAB) were recorded on a JEOL JMS SX/SX102A. Elemental Analysis was performed on an Elementar Vario EL apparatus (Foss Electric). XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with an Al Kα source and a hemispherical analyzer connected to a five-channel detector. Measurements were carried out at 20 eV pass energy. Charging was corrected for by using the C1s peak (284.6 eV) as a reference. Samples were ground and pressed in indium foil, which was placed on an iron stub. The XPS spectra have been fitted with a VGS program fit routine and with XPSPEAK software version 3.1.

Synthesis of *N*-(3-Trimethoxysilane-*n*-propyl)-4,5-bis(diphenylphosphino)phenoxazine (A). A solution of 500 mg (0.907 mmol) of 4,5-bis(diphenylphosphino)phenoxazine in 5 mL of dimethylformamide was added to a suspension of 44 mg (1.833 mmol) of NaH in 5 mL of dimethylformamide. The orange mixture was stirred 90 min at 70 °C. 3-Chloropropyltrimethoxysilane (362 mg; 1.819 mmol) was

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(52) This is in contrast with Rh(**A**) performing as a **Z**-sequence catalyst with which the aldehyde is preferentially reduced. The preference of aldehyde hydrogenation under a CO/H_2 atmosphere has previously been observed on different cationic complexes; see refs 51e and 51g. It is assumed that under hydroformylation conditions aldehyde coordination to the cationic species will be kinetically favored over alkene coordination.

added at room temperature. The mixture was stirred for 18 h at 70 °C. The brown-yellow suspension was filtered and the solvent was removed under reduced pressure. The product was washed with several portions of pentane until an off-white powder was obtained. Solvent and impurities were removed in vacuo (1×10^{-5} bar) at 60 °C for 18 h (Yield 76.9%). Mp 138 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (m, 20H; ArH), 6.66 (t, 2H, $^3J = 7.9$ Hz; CP−C*H*−CH), 6.49 (d, 2H, $^3J = 1.0$ Hz; CH−C*H*−CH), 5.97 (dd, 2H, $^3J = 1.6$, 7.8 Hz; CH−C*H*−CC), 3.61 (s, 9H; CH_3−O), 3.49 (t, 2H, $^3J = 8$ Hz; N−CH_2), 1.80 (m, 2H, $^3J = 8.1$ Hz; CH_2−CH_2−CH_2), 0.72 (t, 2H, $^3J = 8.0$ Hz; Si−CH_2). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, versus H_3PO_4): δ −18.5. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 146.7 (t, *J*(P,C) = 10.9 Hz; CO), 136.8 (t, *J*(P,C) = 12.8 Hz; PC), 133.5 (t, *J*(P,C) = 10.5 Hz; PC*C*H), 132.9 (CN), 128.0 (CH), 127.9 (CH), 124.9 (CH), 124.4 (t, *J*(P,C) = 8.5 Hz; C), 123.5 (CH), 111.6 (CH), 50.4 (CH_3−O), 46.6 (CH_2−N), 17.7 (CH_2−CH_2−CH_2), 5.8 (CH_2−CH_2−Si). ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ −43. FT-IR (KBr): 3058 cm^{-1} (w), 2940 cm^{-1} (w), 2839 cm^{-1} (w), 1553 cm^{-1} (m), 1461 cm^{-1} (s), 1417 cm^{-1} (s), 1377 cm^{-1} (m), 1226 cm^{-1} (m), 1087 cm^{-1} (s), 696 cm^{-1} (s). Exact mass (FAB): 714.2353 [M + 1] (calcd for $C_{42}H_{42}NO_2P_2Si$, 714.2358). Anal. Calcd for $C_{42}H_{41}NO_2P_2Si\ H_2O$: C, 68.93; H 5.92; N, 1.92. Found: C, 69.08; H, 5.70; N, 1.76.

Synthesis of [Rh(B)CO](BF$_4$). Xantphos (**B**) (242 mg; 0.4182 mmol) was added to a clear yellow solution of 80 mg (0.2094 mmol) of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ in 5 mL of EtOH. An orange precipitate was formed and collected by filtration and washed with EtOH and Et_2O (yield 78.5%). The orange compound was dissolved in dichloromethane and 63.6 mg (0.3267 mmol) of $AgBF_4$ was added. A white precipitate was filtered off and the solvent was removed under reduced pressure. The yellow solid compound was recrystallized from dichloromethane/pentane (yield 92.6%). (The triflate analogue was synthesized according to the same procedure). ^{31}P NMR (121.4 MHz, $CDCl_3$, versus H_3PO_4): δ 37.2 (d, *J*(P,Rh) = 121 Hz). ^{1}H NMR (300.0 MHz, $CDCl_3$): δ 7.88 (dd, 2H, ArH), δ 7.66−7.54 (m, 24H, ArH), δ 1.81 (s, 6H, 2Me). FT-IR (KBr): 1997.8 cm^{-1} ν(CO). Exact mass (FAB): 709.0942 [M] (calcd for $C_{40}H_{32}O_2P_2Rh$, 709.0923). Anal. Calcd for $C_{40}H_{32}O_2P_2Rh{\cdot}BF_4{\cdot}0.5CH_2Cl_2$: C 57.99, H 3.97. Found: C 58.68, H 3.90.

Synthesis of Sol−Gel Immobilized [Rh(A)CO]$^+$ ($1_{(I)}{}^+$). A mixture of 5.0 mg (0.0195 mmol) of $Rh(acac)(CO)_2$ and 138.7 mg (0.1946 mmol) of **A** was dissolved in 6 mL of THF. H_2O (2 mL) and 2 mL of TMOS were subsequently added and a red-brown two-phase system was formed. MeOH was added until a clear red-brown solution was formed. Gelation took place within 1 h. After 36 h the gel was carefully dried under reduced pressure. The dried gel was powdered and thoroughly washed with MeOH, THF, and Et_2O. The resulting pink-red silicas were stored at −20 °C. The exact rhodium and phosphine contents of the immobilized catalysts were determined by means of AES. FT-IR (KBr): ν(CO) 2011 cm^{-1}. ^{31}P MAS NMR (121.4 MHz, versus $NH_4H_2PO_4$ = 0.8 ppm): δ 38 br (some phosphine oxide (δ 26) br and protonated phosphine (δ 51) was observed).

Synthesis of Silica Immobilized Catalyst $1_{(II)}{}^+$ to $1_{(V)}{}^+$. A typical catalyst immobilization procedure on silica was used: 2 g of silica (Silica 60 from sds, 70−200 μm, surface area 550 m^2/g), which is stored at 180 °C, was predried at 180 °C under reduced pressure for 2 h. **A** (250 mg; 0.351 mmol) was added to a suspension of the silica in 20 mL of toluene and the resulting mixture was refluxed for 2 h. The silica(**A**) was washed with toluene, dried under reduced pressure, and stored under an inert atmosphere. The silica modification (Scheme 1-III) was performed by refluxing a mixture of 2 g of silica(**A**) and 2 mL of dimethoxydimethylsilane in 20 mL of toluene for 2 h. The resulting modified silica(**A**) was washed with toluene, dried under reduced pressure, and stored under an inert atmosphere.

Catalysts were prepared freshly before use for catalysis. silica(**A**) (1 g) and 1×10^{-5} mol of $[Rh(acac)(CO)_2]$ were stirred in 5 mL of THF for 30 min at room temperature. The resulting catalyst−support system was washed with THF and dried under reduced pressure ($1_{(II)}{}^+$). $1_{(III)}{}^+$ was prepared, on modified silica, similar to method I. To prepare $1_{(IV)}{}^+$, 1 g of silica(**A**) was suspended in a mixture of 1 mL of triethylamine and 5 mL of THF and stirrer at room temperature for 30 min. After 1×10^{-5} mol of $[Rh(acac)(CO)_2]$ was added the reaction mixture was stirred for another 30 min at room temperature. Workup was analogues to other methods. To prepare $1_{(V)}{}^+$, **A** and $[Rh(acac)(CO)_2]$ were stirred in 10 mL of THF for 30 min. Predried silica was added to the yellow reaction mixture and the resulting suspension was stirred for 18 h at room temperature. The resulting yellow-brown catalyst−support system was washed with THF and dried under reduced pressure.

Effect of Silica on HRh(B)(CO)$_2$. CO/H_2 was bubbled through a solution of 5 mg of $[Rh(acac)(CO)_2]$ and 20 mg of **B** in 5 mL of toluene for 10 min. Predried silica (250 mg) was added to the yellow reaction mixture. As a result the solution decolorized and the silica turns orange. FT-IR (KBr): ν(CO) 1972 cm^{-1}. Under continuous bubbling of CO/H_2, 1 mL of 1-propanol was added to the reaction mixture. The solution slowly became yellow. After 20 min a ^{31}P NMR spectrum was acquired: δ 21 (d, *J*(P,Rh) = 125 Hz).

Effect of CF$_3$COOH on HRh(B)(CO)$_2$. CO/H_2 was bubbled through a solution of 5 mg of $[Rh(acac)(CO)_2]$ and 20 mg of **B** in d_6-benzene for 10 min. CF_3COOH (20 μL) was added to the reaction mixture under continuous bubbling of CO/H_2. ^{31}P NMR: δ 38 (br d, *J*(P,Rh) = 111 Hz). A hydroformylation and a hydrogenation experiment were performed using a catalyst mixture of 1×10^{-5} mol of $[Rh(acac)(CO)_2]$, 1×10^{-4} mol of **B,** and 20 μL of CF_3COOH in toluene (see below for details).

Hydroformylation of 1-Octene. A typical catalysis experiment was used: A stainless steel 50 mL autoclave, equipped with a mechanical stirrer, a substrate vessel, a cooling spiral, and a sample outlet was charged with 1 g of 1×10^{-5} mol rhodium catalyst containing silica in 10 mL of toluene. The suspension was incubated for 1 h at 80 °C under 20 bar of CO/H_2 (1:1). A mixture of 1 mL of 1-octene and 1 mL of decane in 3 mL of toluene was added and the CO/H_2 pressure was brought to 50 bar. The mixture was stirred for 24 h. The autoclave was cooled to 10 °C and the pressure was reduced to 1.8 bar. With this small overpressure the liquid is slowly removed from the catalyst with a 1.2 mm syringe. After the catalyst was washed with 5 mL of toluene, 10 mL of toluene is added and the pressure was brought to 20 bar. Finally the mixture was heated to 80 °C and the second cycle was performed.

Switching of Catalyst Functionality. Hydroformylation−reduction sequence reactions were performed as described above. Hydroformylations were also performed under the same conditions, but 1 mL of propanol was added to the reaction mixture. Hydrogenations were performed on a reaction mixture of 1 mL of 1-octene, 1 mL of 1-nonanal, and 1 mL of decane in 12 mL of toluene under 50 bar of H_2 at 80 °C. The catalyst recycling procedure was performed as described above.

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