Improved Rhodium Hydrogenation Catalysts Immobilized on Oxidic Supports

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Abstract: Wilkinson-type rhodium hydrogenation catalysts immobilized on oxidic supports *via* mono- and bidentate phosphine linkers have been studied by ^{31}P solid-state NMR, and their recycling stability and lifetime with respect to hydrogenation of 1-dodecene, 2-cyclohexen-1-one, and 4-bromostyrene have been improved substantially.

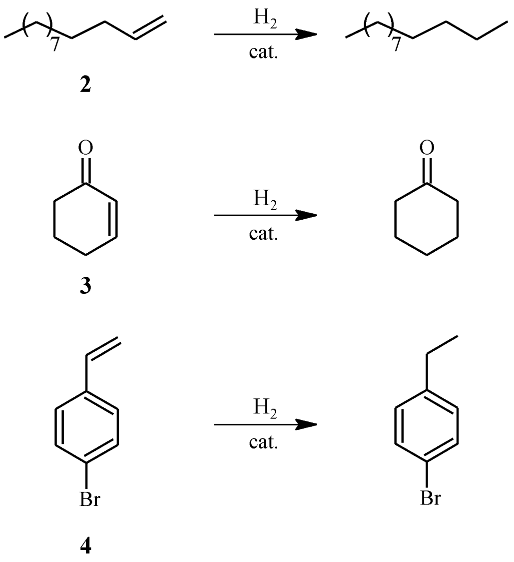
Keywords: alkene reduction; catalytic hydrogenation; immobilization; P ligands; rhodium; silica; solid-state NMR

The immobilization of homogeneous catalysts[1] *via* linkers on supports is of growing importance because it allows an easy separation of the catalyst from the reaction mixture as well as its recycling.[2,3] For some time our group, like others, has pursued this idea by immobilizing homogeneous rhodium and nickel catalysts on inorganic oxidic supports *via* bifunctional phosphine linkers such as $Ph_2P(CH_2)_3Si(OEt)_3$ (**1**).[4–7] The main disadvantage of immobilized catalysts has always been leaching, the uncontrolled detachment of the metal fragment from the support, with or without the linker. Over time, we could identify and eliminate some sources of leaching. First of all, one has to prevent the oxidation of the phosphine by the combined action of the silica surface and the ethoxysilane groups during the immobilization step.[4] Then, the proper support material has to be chosen. In order to get strong covalent and irreversible bonding of the ethoxysilane group, well-dried silica[8,9] is best suited, while titania or magnesia lead to persistent linker leaching.[10] Since monodentate phosphines do not necessarily bind the metals to the support in a chelating manner,[11] chelating phosphines have been designed,[12] which should also provide a stronger metal-ligand bonding.[7] These ligands[12] additionally allow one to study the dependence of catalytic activity on their bite angles and spacer lengths. All the amorphous surface-modified materials are best studied with our improved analytical methods of optimized classical solid-state NMR[13] and suspension NMR.[10,14]

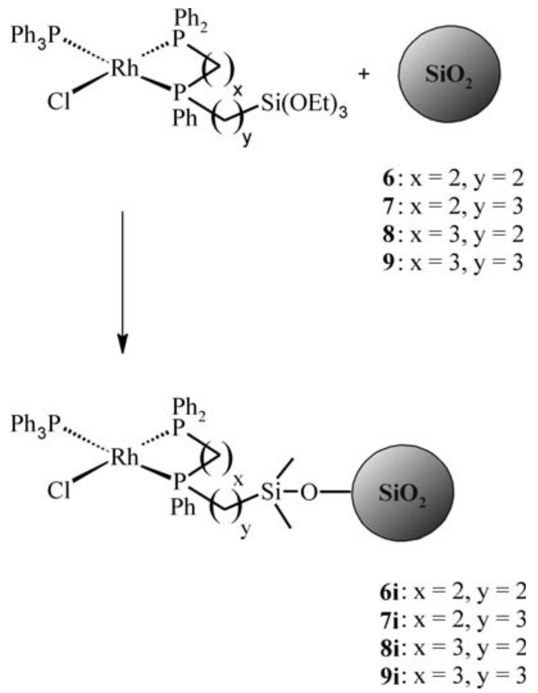
In this contribution we will demonstrate that the efficiency, stability and lifetimes of surface-bound Wilkinson-type rhodium catalysts for olefin hydrogenation, one of the most important and best developed areas of catalysis,[15] can be improved substantially by simple measures, namely the proper choice of pore diameter and surface coverage of the support, as well as using chelating ligands.

For the easy comparison of the hydrogenation characteristics with our previous results,[6] and those of other groups,[16] we used the standard set of substrates for the catalytic runs, 1-dodecene (**2**), 2-cyclohexen-1-one (**3**), and 4-bromostyrene (**4**). In the work presented here, all the substrates **2**–**4** were selectively hydrogenated, and dodecane, cyclohexanone, and 4-bromoethylbenzene were the only products (Scheme 1).

The rate of conversion was determined by NMR and GC analysis. The complex $ClRh[PPh_2(CH_2)_3Si(OEt)_3]_3$ (**5**) was synthesized starting from the precursor $[(COD)RhCl]_2$, characterized and immobilized to give **5i** as described previously.[6] The chelate complexes **6**–**9** (Scheme 2) were obtained by reaction of $Cl(PPh_3)Rh(COD)$ with the corresponding chelating



Scheme 1. Hydrogenation of **2**–**4** with homogeneous (**6**–**9**) and immobilized (**6i**–**9i**) catalysts.



Scheme 2. Immobilization of rhodium catalysts by chelating linkers.

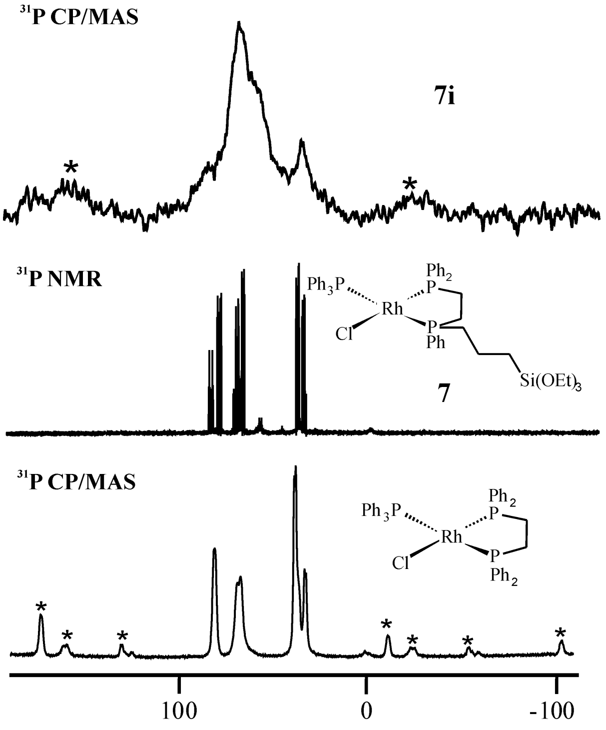


Figure 1. 162.0 MHz ^{31}P CP/MAS spectra of amorphous **7i** (top, rotational frequency 13 kHz) and polycrystalline $Cl(PPh_3)Rh(dppe)$ (bottom, spinning speed 15 kHz); spinning sidebands are denoted by asterisks, other measurement parameters, see ref.[13] Middle spectrum: 121.5 MHz $^{31}P\{^1H\}$ NMR spectrum of **7** in THF.

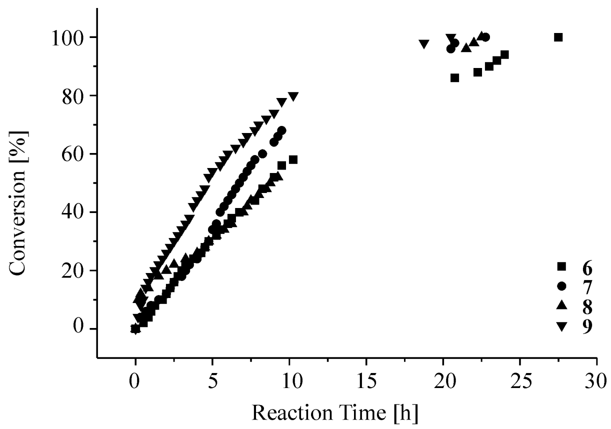


Figure 2. Hydrogenation of 4-bromostyrene (**4**) with catalysts **6**–**9** in toluene at 60 °C, with a catalyst to substrate ratio of 1:100.

phosphines.[12] Every unsymmetrical chelating ligand leads to two inseparable isomers of the square-planar complexes in a statistical ratio. However, as will be elaborated in a future paper,[17] both isomers are equally active hydrogenation catalysts, so that we can safely apply the mixtures here. Immobilization of **6**–**9** on silica (see Experimental Section), using the standard procedure[6] after their full characterization[18] gave the surface-bound versions **6i**–**9i** (Scheme 2).

The success of all the immobilizations can be demonstrated by ^{31}P CP/MAS NMR[13] of the resulting materials. The top spectrum in Figure 1 shows the signals of **7i**. Due to the more inhomogeneous surroundings of the phosphorus nuclei on the silica surface the lines are broader than the ones in solution (**7**, middle spectrum, Figure 1) or in the spectrum of the analogous polycrystalline complex[19] $Cl(PPh_3)Rh(dppe)$ (bottom spectrum). The signal intensities of the isotropic lines of **7i** and of the polycrystalline complex are different from the solution NMR signals of **7** in THF, because each signal has its own chemical shift anisotropy[20] (CSA). The larger the CSA, the more signal intensity is found in the rotational sidebands at the expense of the isotropic line. Nevertheless, it is obvious that no uncomplexed phosphines[12] or oxidic species[4] are present.

As we could show previously, the efficiency of the immobilized catalyst **5i** is comparable to that of **5**.[6] In order to demonstrate that this is also true for all substrates and for the rhodium catalysts with chelating ligands, we compared the catalytic activities of the catalysts **6**–**9** with those of **5i** and **6i**–**9i** on silica. As expected, the catalysts with chelating ligands need slightly higher temperatures (60 °C) for the hydrogenations than **5** or **5i** (25 °C). Interestingly, as shown for bromostyrene (**4**) and cyclohexenone (**3**) as the substrates in Figures 2 and 3, the bite angles of the phosphines or the spacer lengths do not make a crucial difference with respect to the efficiency of the homogeneous hydrogenation, irrespective of the substrate. The

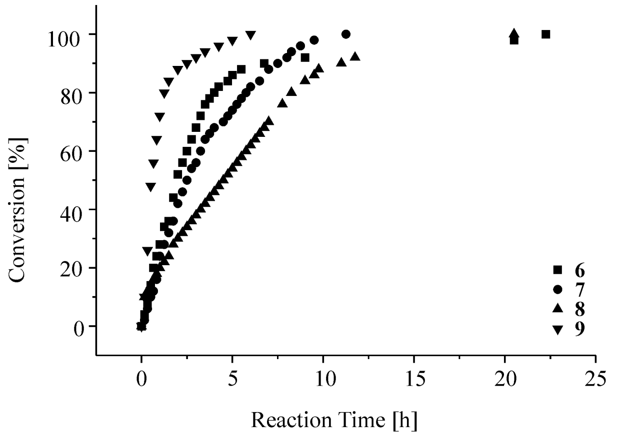


Figure 3. Hydrogenation of cyclohexenone (**3**) with the catalysts **6**–**9** in toluene at 60 °C, with a catalyst to substrate ratio of 1:100. Details of the experimental setting see ref.[6]

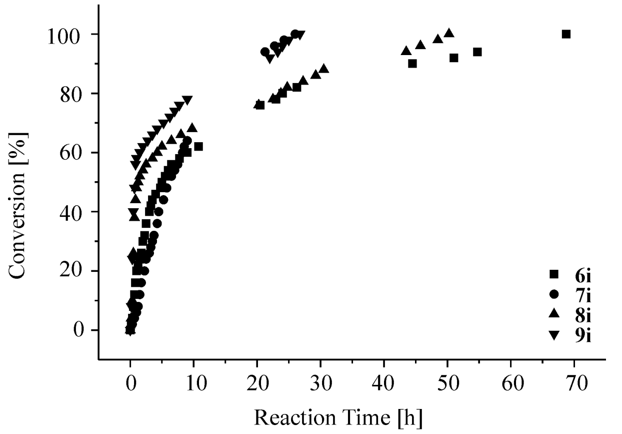


Figure 4. Hydrogenation of cyclohexenone (**3**) with the silica-bound catalysts **6i**–**9i** in toluene at 60 °C, with a catalyst to substrate ratio of 1:100. Details of the experimental setting see ref.[6]

difference in activity of the catalysts with various ligands is even smaller in the case of **6i**–**9i** (Figure 4). On going from **6**–**9** to the immobilized versions **6i**–**9i** the reaction times increase to about two to three times the original values, because now the substrates have to diffuse into the pores of the solid support (see also below). However, this disadvantage is made up for by the possibility of recycling. All catalysts **6**–**9** and **6i**–**9i** give 100% conversion and optimal selectivity for all substrates **2**–**4**. Although every one of the catalysts **6i**–**9i** is useful and each has its merit for one special catalytic setting, overall however, the catalysts **9** and **9i** show generally very good performance for all olefins, and might be tried first for different reactions by other groups.

All the chelating ligands improve the lifetimes of the immobilized catalysts substantially, which was to be expected regarding the results of a parallel project with nickel catalysts.[7] While monodentate phosphine ligands in the case of dodecene as the substrate only allowed the batch-wise recycling of the rhodium hydrogenation catalysts for seven times,[6] with the catalysts **6i**–**9i** 100% conversion is reached for all substrates in every one of the 13 cycles. This is for example shown with **6i** on silica and **2** as the substrate in Figure 5. Therefore, we conclude that our chelating ligands generally, even for very different metal moieties,[7] lead to diminished leaching and thus to improved stabilities and lifetimes of immobilized catalysts.

Since it is known for rhodium catalysts that dimerization leads to unreactive species,[21] we sought to improve our catalysts further by diluting them on the silica surface, and thus keep the reactive metal centers apart from each other – one of the additional options that immobilization offers in contrast to homogeneous catalysis. Indeed, as can be seen in Figure 6 for **5i** on silica and **2**, when the surface coverage is decreased stepwise from the maximal coverage m to half the surface coverage (m/2), then to m/4, and finally to m/10, the turnover frequency (TOF) in a single run increases substantially. The improvement is greatest on going from m to m/2 and m/4, when the time requirement for 100% conversion decreases from 17 h to about 9 h (see also Table 1). Diluting **5i** further to m/10, however, only saves roughly another half hour. Therefore, we conclude that as soon as the active metal centers are far enough apart from each other, a condition reached here at m/4, no dimerization is possible any more and the maximal lifetime of the catalyst with respect to this dimerization deactivation mechanism is reached. Further dilution to m/10 is unnecessary and only increases the bulk material of the support, leading to "dead reactor volume" in potential industrial applications. The same observation is made for immobilized nickel catalysts,[7] and all our catalysts with chelating ligands.[17]

The fact that the change of the surface coverage of the complexes also affects the catalytic activity furthermore corroborates the assumption that during the immobilization step the metal centers are distributed evenly on the surface, and do not settle down in patches. This is another proof that with rigorously dried silica (see above), which contains no more adsorbed water and only few isolated Si-OH groups,[22] no cross-linking of the ethoxysilane groups can take place,[8,9] and therefore no "clustering" of the metal centers. Cross-checking this result with silica, which was only dried at 25 °C and should therefore be wet enough to allow cross-linking, leads to a loss of catalytic activity (Figure 6).

As long as the inorganic oxidic supports are dried rigorously, by dilution of the metal centers on the surface one can also improve those catalysts immobilized *via* phosphine linkers, for example, on alumina (Table 1). Going from maximal surface coverage m of **5i** to m/10 reduces the time required for hydrogenating **2** from 48 h to about 10 h.

The advantageous effect of diminished surface coverage is independent of the average pore diameter of the

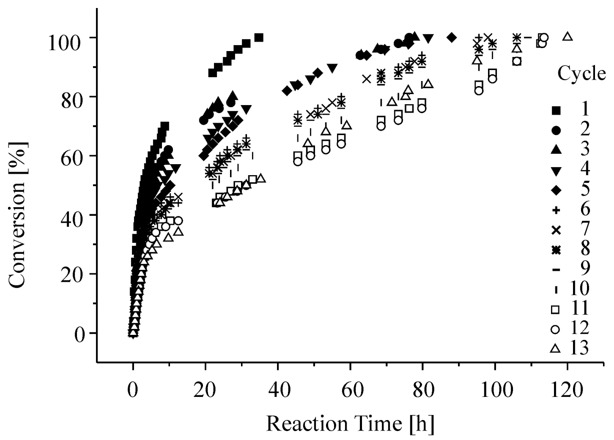


Figure 5. Batch-wise recycling of the catalyst: hydrogenation of dodecene (**2**) with **6i** on silica at 60 °C in toluene with a catalyst to substrate ratio of 1:100. Details of the experimental setting see ref.[6]

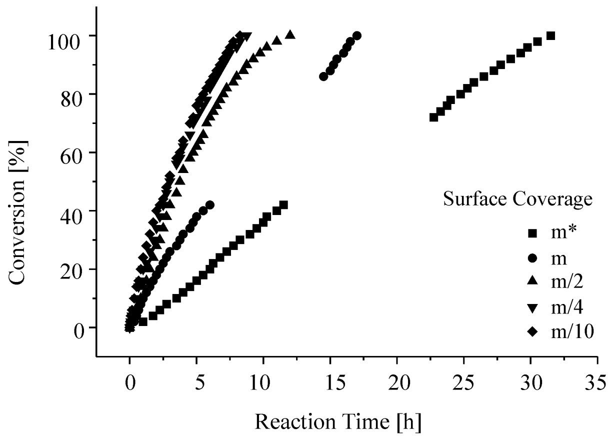


Figure 6. Hydrogenation of dodecene (**2**) by **5i** on SiO_2 (40 Å). m denotes maximal surface coverage (0.10 mmol **5** on 1 g of SiO_2); the asterisk denotes maximal surface coverage of **5i** on silica dried in vacuum at ambient temperature; catalyst to substrate ratio 1:100; details of the experimental setting see ref.[6]

support, as can be seen in Table 1 for values between 40 and 100 Å. Larger pores should allow better diffusion of bulky substrates to the innermost catalytic centers. Indeed, dodecene can be hydrogenated with **5i** on SiO_2 (100 Å) in only half the time required for **5i** on SiO_2 (40 Å) as the support. This result is also displayed for the catalytic system **5i**/**2** in Figure 7. With more compact substrates, such as **3** or **4**, this effect is less pronounced. For example, for **5i**/**3** the gained time difference is only 1.4 h (Table 1).

Since the linkers are bound covalently to the support, and unlike merely physically adsorbed species[8,10] they cannot migrate on the surface, the dilution of the metal centers is persistent. Therefore, it is not surprising that dilution also enhances the lifetime of **5i**, when the catalyst is recycled in a batch-wise manner. Figure 8 shows convincingly that the effect of catalyst dilution on the surface even overrides the advantages of chelate bonding. With **5i** quantitative conversion of **2** is obtained already after 100 h in the 13th run, while 120 h are needed with **6i** immobilized with maximal density on the support (Figure 5). Combining all the advantageous effects of optimal support, surface coverage, and chelating linkers will be the subject of further investigations.[17]

Table 1. The effects of different supports and surface coverages with **5i** on the time required for quantitative conversion of **2** to dodecane, and of **3** to cyclohexanone. Numbers in brackets give the average pore diameters; #alumina with neutral surface;[10] *silica dried at 25 °C under vacuum; m denotes maximal surface coverage.

Support for **5i**	Surface Coverage	Time for 100% Conversion [h]	
		1-Dodecene	2-Cyclohexen-1-one
Al_2O_3 (90 Å)#	m	48.0	39.7
	m/4	11.7	11.0
	m/10	9.7	10.5
SiO_2 (40 Å)*	m	31.5	29.5
SiO_2 (40 Å)	m	17.0	13.3
	m/2	12.0	9.5
	m/4	8.7	9.0
	m/10	8.3	8.7
SiO_2 (60 Å)	m	17.3	14.5
	m/2	11.7	10.5
	m/4	7.7	9.5
	m/10	7.3	9.5
SiO_2 (100 Å)	m	18.0	15.0
	m/2	13.0	9.0
	m/4	5.0	7.7
	m/10	4.3	7.3

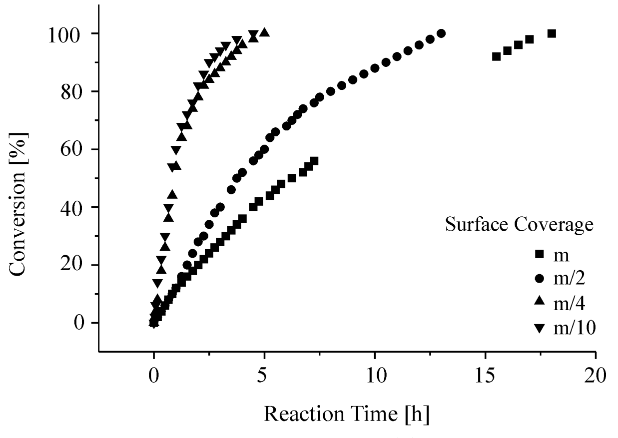


Figure 7. Hydrogenation of dodecene (**2**) by **5i** on silica with an average pore diameter of 100 Å in toluene. m denotes maximal surface coverage (0.05 mmol **5** on 1 g of SiO_2); catalyst to substrate ratio 1:100; details of the experimental setting see ref.[6]

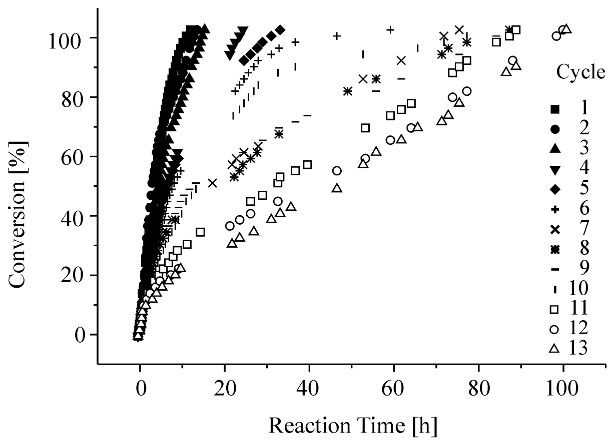


Figure 8. Batch-wise recycling of the catalyst. Hydrogenation of dodecene (**2**) with **5i** on SiO_2 (40 Å) in toluene with half-maximal surface coverage m/2 (0.05 mmol **5** on 1 g of SiO_2) and a catalyst to substrate ratio of 1:100; details of the experimental setting see ref.[6]

In conclusion, we have demonstrated that even simple measures can improve the efficiency, stability, and lifetime of immobilized catalysts. These results are of a general nature with respect to different catalytic reactions, metal centers, substrates, linkers, supports, surface coverages and pore diameters. They clearly further extend the utility of immobilized catalysts derived from the covalent linkage of homogeneous metal complexes to oxidic supports.

Experimental Section

All catalytic reactions were performed under inert gas using Schlenk techniques, prior to admitting hydrogen. If not stated otherwise, silica with 40 Å average pore diameter, 750 m^2/g surface area, and a particle size of 0.063 to 0.2 mm was dried at 600 °C under vacuum for 24 h prior to use and stored under N_2. All catalysts were immobilized according to the standard procedure given in ref.[6] The details of the solid-state NMR measurements are given in ref.[13]

Acknowledgements

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