Comparison between homogeneous and sol–gel-encapsulated rhodium-quaternary ammonium ion pair catalysts

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Abstract

The ion pairs $RhCl_3$/Aliquat 336[®] and $RhCl_3$/[$Me_3N(CH_2)_3Si(OMe)_3$]Cl were entrapped in SiO_2 sol–gel matrices, and used as catalysts for isomerization of allylbenzene, disproportionation of 1,3-cyclohexadiene, hydrogenation of alkenes, alkynes, arenes, nitriles and nitro-compounds, and for hydroformylation of C–C double bonds. The immobilized ion pairs proved to be stable, leach-proof and recyclable. Occasionally the catalytic efficiency dropped upon recycling, owing to pore blockage but the activity could be restored by treatment with boiling water. The performances of the sol–gel-entrapped ion pairs were compared with those of the homogeneous $RhCl_3$/Aliquat 336 catalyst. In most cases the immobilized catalysts proved superior to their homogeneous version.

Keywords: Immobilized catalysts; Hydroformylation; Hydrogenation; Rhodium; Sol–gel

1. Introduction

Ion pairs generated from $RhCl_3 \cdot 3H_2O$ and quaternary ammonium salts have already been shown to catalyze under phase transfer conditions (i) double bond migration in allylic compounds, (ii) disproportionation and dehydrogenation of cyclic dienes, (iii) selective transfer of hydrogen from silicon hydride donors to alkynes, alkenes, unsaturated carbonyl- and nitro-compounds, (iv) room temperature hydrogenation of olefinic, acetylenic and aromatic C–C bonds, (v) cyclooligomerization and cyclorearrangement of mono- and dialkynes, and addition of water, carbon monoxide, sulfur and some other active diynophiles to a variety of acetylenes [1]. The used rhodium catalysts in processes (i)–(iii), as well as in the hydration of acetylenes, could be recovered in part (though not entirely) in the aqueous phase as water soluble rhodium salts, by treatment of the reaction mixtures with lipophilic salts ($NaClO_4$, $NaBPh_4$) [2–5]. In the other processes, however, the ion pairs were transformed during the catalysis to non-recyclable complexes. We have demonstrated recently [6] that these versatile ion pairs can be converted into truly recyclable long lasting catalysts, by their entrapment in SiO_2 sol–gel matrices [7]. The room temperature con-

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ditions under which these matrices can be formed from tetraalkoxysilanes have already proven suitable for encapsulation of various organic, bioorganic and organometallic compounds, in ceramic materials [8]. This opens, in fact, the possibility of heterogenizing of many reactions which traditionally have been carried out under homogeneous conditions [3]. In this study we report the encapsulation of RhCl$_3$-quaternary ammonium ion pair catalysts, and demonstrate their utility in some isomerization, disproportionation, hydrogenation and hydroformylation processes.

2. Experimental

2.1. Preparation of the entrapped catalysts

Typically, a mixture of 20 mg (8.23×10^{-3} mmol) RhCl$_3 \cdot 3H_2O$ and an equimolar amount of the appropriate quaternary ammonium salt in 2.4 ml of triply distilled water was stirred in a cylindrical vial (diameter 2 cm) at 25°C for 10 min. Methanol (3.5 ml) was added and the stirring was continued for 30 min. If the solution was not completely homogeneous (as in the case where Aliquat 336® served as the quaternary ammonium salt) the mixture was heated briefly to 60°C to ensure complete dissolution. Tetrametoxysilane (2.5 ml) was added (silane:water = 1:8), the stirring was continued for 10 min, and the mixture was left to stand at 25° for 3–4 days until gelation was completed. The mixture was heated at 45°C until constant weight was achieved. The catalyst was washed with 20 ml of boiling CH$_2$Cl$_2$, sonicated for 30 min in the same solvent, dried for 3 h at 1 mm, washed with 20 ml of boiling triply distilled water, and dried at room temperature at 1 mm for 20 h before use. The exact rhodium content of the sol–gel catalyst was determined by substraction of the rhodium content in the combined washings (analyzed by atomic absorption [9]) from the original amount of metal employed.

2.2. Isomerization of allylbenzene

A reaction flask equipped with a reflux condenser, a magnetic bar and a rubber sealed side arm was charged with the catalyst material and 3 ml of toluene. The vessel was placed in an oil bath thermostated at 90°C. After temperature equilibration, 270 mg (2.3 mmoles) of allylbenzene was injected into the flask. At intervals of 1–10 min, 2-μl samples were withdrawn and frozen to await GC analysis on a 2-m long column packed with Carbowax 20 M on Chromosorb W, operated at 100°C).

Upon completion of the reaction the liquid was decanted and analyzed for leached rhodium by atomic absorption. The catalyst was washed with 20 ml of boiling CH$_2$Cl$_2$, sonicated for 30 min, washed again with the same amount of solvent and dried for 3 h at 1 mm. The dried catalyst was used in a second run. If the reactivity of catalyst decreased, the CH$_2$Cl$_2$ washings were followed by treatment ($2 \times$) with 20 ml of boiling water followed by drying for 20 h at 1 mm.

2.3. Disproportionation of 1,3-cyclohexadiene

The catalyst and 2 ml of toluene were placed in a reaction flask as above. After temperature equilibration, 2 mmol of 1,3-cyclohexadiene was injected into the flask and samples were withdrawn periodically. Product analysis was carried out on a 3-m long GC column packed with 20% DEGS on Chromosorb W, operated at 30°C. Catalyst recovery was performed as described above.

2.4. General procedure for hydrogenation experiments

A catalyst containing 8.2×10^{-3} mmol of the ion pair, a magnetic bar, 2 mmol of the unsaturated substrate (usually together with a saturated hydrocarbon as internal standard) and 2 ml of CH$_2$Cl$_2$ were placed in a glass lined mini autoclave. The apparatus was sealed,

washed (3 ×) with hydrogen, and charged with the same gas at the desired pressure. After the required length of time the reaction vessel was cooled, and its content analyzed both by GC and NMR. Metal leaching analysis and catalyst recovery was performed as described above.

2.5. General procedure for hydroformylation experiments

In a mini autoclave with stirring and sampling devices were introduced a catalyst containing 8.2×10^{-3} mmol of rhodium, 5 mmol of substrate and 2 ml of toluene. The reaction vessel was flushed with hydrogen and CO and refilled with 300–400 psi of each H_2 and CO, and heated by an electronically controlled heating mantle at the desired temperature. Samples were withdrawn periodically from the autoclave and analyzed by GC, GC–MS and/or NMR. Leaching analysis and catalyst recycling were performed in the manner described above.

3. Results and discussion

Two kinds of rhodium-quaternary ammonium ion pair catalysts have been entrapped in sol–gel matrices: (i) ion pairs with no functional groups that may bind covalently to the silica support, and (ii) ion pairs with a silyloxy group that can copolymerize with the matrix's starting material — tetramethoxysilane. The encapsulated $RhCl_3$/Aliquat 336 couple (catalyst **1**), which is formed by addition of the components of the ion pair to the $Si(OMe)_4$ during the polymerization process, is an example of the physically encapsulated catalyst (cf. ref. [10]). For the preparation of a catalyst that is chemically bound to the sol–gel backbone [11–13], we copolymerized $Si(OMe)_4$ with $[Me_3N(CH_2)_3Si(OEt)_3]Cl$ (purchased from ABCR, Karlsruhe, Germany), in the presence of $RhCl_3 \cdot 3H_2O$ (catalyst **2**).

Application of catalysts **1** and **2** in some double bond migration, disproportionation, hy-

drogenation and hydroformylation processes revealed that in spite of the different mode of entrapment, both are practically leach proof, and could be utilized repeatedly in numerous runs. In some cases, however, each of the entrapped ion pairs catalyzed reactions in different rates and sometimes even let to different products.

We have already shown [6] that the encapsulation of $RhCl_3$ in a sol–gel matrix either in the presence or absence of cetyltrimethylammonium bromide, forms catalysts which are not only recyclable, but promote substantially faster double bond migration in allylic compounds than non-immobilized $RhCl_3 \cdot H_2O$. These catalysts were shown e.g., to convert allylbenzene into an equilibrium mixture with *cis* and *trans*-(3-propenyl)benzene (Eq. 1) almost twice as fast as the soluble $[(C_8H_{17})_3NMe]^+[RhCl_4 \cdot nH_2O]^-$ ion pair (that reacts under phase transfer conditions [2]).

$$PhCH_2CH=CH_2$$

$$\rightarrow \textit{cis- and trans-}PhCH=CHMe \qquad (1)$$
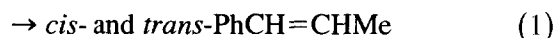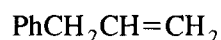
We have now found that the sol–gel entrapped $RhCl_3$/Aliquat 336 catalyst is even more active, and completes reaction (1) within 2 h (as compared to 4 h by its homogeneous version). However, some dirhodium complexes that have built-in quaternary ammonium moieties, such as $[Rh(CO)(Ph_2PCH_2CH_2NMe)(\mu\text{-}S\text{-}CMe_3)]_2^{2+}[BPh_4]_2^{2-}$ [14] were found to lose their activity as isomerization catalyst, upon encapsulation.

In contrast to the isomerization reaction that could be carried out also in the absence of an entrapped quaternary ammonium salt, the following disproportionation, hydrogenation and hydroformylation processes required the presence of the onium moiety.

Disproportionation of 1,3-cyclohexadiene (Eq. 2) was shown to proceed equally well by **1**

$$2C_6H_8 \rightarrow C_6H_{10} + C_6H_6 \qquad (2)$$
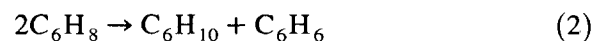
and **2**. Under the conditions given in the Experimental section, the respective conversions after 40 min were 97 and 96%. Disproportionation of

the diene in a two liquid phase system of toluene and water could be carried out also by the non-immobilized $RhCl_3$/Aliquat 336 catalyst, but the rate was slower [4]. Under complete homogeneous conditions in water-free toluene the soluble ion pair proved inactive.

Catalyst 1 and 2 could be recycled in numerous runs with hardly any loss in activity provided the sol–gel glasses were treated between the runs with boiling CH_2Cl_2 followed by sonication in order to open blocked pores. Experiments conducted with sol–gel-entrapped $RhCl_3$ and $[Bu_4N]Cl$ instead of $RhCl_3$/Aliquat 336 resulted in slow leaching of the small ammonium salt and gradual deterioration of the catalyst. Thus, the conversion of 1,3-cyclohexadiene

with this catalyst after 90 min were in the first four runs 93, 89, 71 and 30%, respectively.

The disproportionation reaction by 1 and 2 could be applied to other dienes as well. The results of these studies will be disclosed in a separate paper.

In analogy to the soluble $RhCl_3$/Aliquat 336 catalyst, 1 and 2 promote hydrogenation reactions as well. The heterogenized catalysts require, however, a somewhat higher pressure of H_2, but are substantially more stable and can be fully recycled. Unlike the soluble catalysts that operate under phase transfer conditions, 1 and 2 can be employed in various water-free organic solvents. While the homogeneous catalyst has to be stabilized by trioctylamine to avoid precipita-

Table 1
Hydrogenation of several unsaturated compounds by the sol–gel entrapped ion pair catalysts 1 and 2 at 50°C [a]

Expt.	Substrate	Catalyst	H_2 pressure (psi)	Reaction time (h)	Products (yield 1st run, %)
1	styrene	1	120	1	ethylbenzene (100)
2	styrene	2	120	4	ethylbenzene (48)
3	t-stilbene	1	120	4	bibenzyl (35)
4	t-stilbene	2	120	4	bibenzyl (64)
5	benzalacetone	1	120	3	4-phenylbutan-2-one (62)
6	benzalacetone	2	120	3	4-phenylbutan-2-one (72)
7	phenylacetylene	1	120	4	styrene (72), ethylbenzene (20)
8	phenylacetylene	2	120	4	styrene (18), ethylbenzene (3)
9	benzene	1	120	4	cyclohexane (100)
10	benzene	2	120 [b]	15	cyclohexane (68)
11	acenaphthylene	1	120	4	acenaphthene (85)
12	acenaphthylene	2	120	4	acenaphthene (54)
13	naphthalene	1	240	18	tetralin (33), c-decaline (66) [c]
14	naphthalene	2	240	18	tetralin (32), c-decaline (66) [c]
15	1-naphthol	1	140	18	5-hydroxytetralin (24)
16	1-naphthol	1	400	18	c-decaline (12), t-1-hydroxydecaline (37), t-1-decalone (51)
17	1-naphthol	2	140	18	1-hydroxytetralin (13), 5-hydroxytetralin (56), 1-tetralone (13)
18	1-naphthol	2	400	12	c-1-hydroxydecalin (52), c-1-decalone (47)
19	benzyl bromide	1	120	18	toluene (53)
20	benzyl bromide	2	120	18	toluene (60)
21	(3-bromopropyl)-benzene	2	500	12	(3-bromopropyl)cyclohexane (50)
22	nitrobenzene	1	120	4	aniline (34)
23	nitrobenzene	2	120	4	aniline (50), aminocyclohexane (50)
24	Benzonitrile	1	400 [d]	4	benzylamine (98)
25	benzonitrile	2	400 [d]	4	benzylamine (88)

[a] Reaction conditions as in the Experimental section.
[b] At 100°C.
[c] And < 1% t-decaline.
[d] At 100°C.

tion of inactive material [15] the sol–gel entrapped ion pairs do not need any additive to prevent deterioration.

The hydrogenation experiments summarized in Table 1 indicate that the relative catalytic activity of 1 and 2 varies from one substrate to another. While e.g., 1 is a much better catalyst for the hydrogenation of styrene than 2, the latter is more active than 1 in the conversion of *trans*-stilbene into bibenzyl. At 50°C and 120 psi H_2, terminal and internal olefins, as well as α,β-unsaturated ketones are smoothly hydrogenated within a few hours. Under these conditions benzene is transferred in quantitative yield to cyclohexane by 1 but not by 2. In the presence of the chemically-bound sol–gel entrapped catalyst, the reduction of benzene at 50°C and 120 psi is extremely slow. Only at 110°C the rate becomes appreciable, and 68% of cyclohexane is obtained after 15 h. In substrates which have both olefinic and aromatic C–C bonds (e.g., acenaphthylene) only the non-aromatic bond is hydrogenated at 120 psi.

In general, the higher arenes require an increase in H_2 pressure. At 240 psi naphthalene is converted within 18 h by both catalysts into a 1:2 mixture of tetralin and *cis*-decaline. Slow selective hydrogenation of just one ring takes place by 1 at 140 psi. At this pressure 1-naphthol is reduced solely at the non-substituted ring to give 5-hydroxytetralin. Catalyst 2 is less selective under these conditions, and forms also 1-hydroxytetralin and 1-tetralone (the latter can be regarded as the keto-tautomer of 1-hydroxy-3,4,4a,5,6,7,8,8a-octahydronaphthalene). At 400 psi, 1 (but not 2) catalyzes partial hydrogenolysis of the OH group and promotes the reduction of both aromatic rings to give *trans*-1-hydroxy-decaline and *trans*-decalone. Catalyst 2 does not induce hydrogenolysis. It promotes the formation of 1-hydroxytetralin as well as 1-decalone with the *cis* orientation.

Under phase transfer conditions the homogeneous $RhCl_3$/Aliquat 336 ion pair causes hydrogenolysis of both aromatic and aliphatic halogen atoms [1]. At 120 psi H_2 the sol–gel entrapped catalysts neither affected aromatic halogen atoms (chlorobenzene, bromonaphthalenes) nor side chain bromides, except that of benzyl bromide which yielded toluene. (3-Bromopropyl)benzene was neither hydrogenated by 1 nor by 2 at 120 psi H_2. At 500 psi the chemically-bound catalyst 2 (but not 1) promoted slow reduction of the aromatic ring without affecting the bromine. Nitrobenzene was hydrogenated at 120 psi by both catalysts. How-

Table 2
Hydroformylation of some olefins by the sol–gel entrapped ion pair catalysts 1 and 2 [a]

Expt.	Substrate	Catalyst	Reaction temp (°C)	Total pressure (psi)	Reaction time (h)	Products (yield in 1st run, %)
1	cyclopentene	1	105	600	6.5	C_5H_9CHO (95)
2	cyclopentene	2	105	600	6.5	C_5H_9CHO (50)
3	cyclohexene	1	134	600	4.5	$C_6H_{11}CHO$ (94)
4	cyclohexene	2	134	600	13.5	$C_6H_{11}CHO$ (8)
5	1-decene	2	85	600	4	$Me(CH_2)_9CHO$ (41), $Me(CH_2)_7CH(CHO)Me$ (41), $Me(CH_2)_6CH(CHO)Et$ (8), $Me(CH_2)_5CH(CHO)Pr$ (8)
6	styrene	1	80	600	6	$Ph(CH_2)_2CHO$ (68), $PhCH(CHO)Me$ (31)
7	styrene	2	80	600	6	$Ph(CH_2)_2CHO$ (59), $PhCH(CHO)Me$ (27)
8	1-methylstyrene	1	110	800	21.5	$PhCH(Me)CH_2CHO$ (12)
9	1-methylstyrene	2	110	800	21.5	$PhCH(Me)CH_2CHO$ (85)
10	allyl phenyl ether	2	84	600	21	$PhO(CH_2)_3CHO$ (37) [b]

[a] Reaction conditions as in the Experimental section.
[b] In addition to 19% of starting material there was also isolated 15% 1-butanal, 1% 2-butanal and 15% phenol.

ever, while **1** formed soly aniline, **2** yielded also aminocyclohexane. It should be recalled that under phase transfer conditions the homogeneous ion pair forms in addition to aniline also nitrocyclohexane [16]. Benzonitrile that is not hydrogenated under homogeneous conditions could be transformed to benzylamine at 400 psi and 80–100°C. When the drying of catalyst **2** from the water washings was incomplete, the nitrile was reduced (at 200 psi and 80°C) to PhCH=NH which readily underwent hydrolysis to PhCHO.

Although the soluble $RhCl_3$/Aliquat 336 ion pair was shown to catalyze the carbonylation of several diynes [1,17], it proved unsuitable as a hydroformylation catalyst. The sol–gel encapsulated version **1**, as well as catalyst **2** have now been found applicable to such processes. Some representative results are summarized in Table 2. As in the hydrogenation reactions, the catalysts vary in their activity: sometimes **1** has the higher activity and sometimes vice versa. At 100–135°C, 300 psi H_2 and 300 psi CO, cyclopentene and cyclohexene form in toluene the corresponding cyclic carboxaldehydes. Catalyst **1** is preferred in these reactions. Linear alkenes such as 1-decene have been shown to undergo double bond migration as a side reaction and consequently mixtures of aldehydes are formed. The products obtained from 1-decene were in addition to $Me(CH_2)_9CHO$ and $Me(CH_2)_7CH(CHO)Me$ also $Me(CH_2)_6CH(CHO)Et$ and $Me(CH_2)_5CH(CHO)Pr$. Styrene gave a mixture of the expected linear and branched aldehydes. The ratio b:l could be increased by lowering the temperature, albeit at the expense of the reaction rate. Substitution of the toluene by benzene led, in the **1**-catalyzed reaction, to an increase of the b:l ratio from 2.2 to 3.4, but decreased the ratio in the **2**-catalyzed process from 2.2 to 1.5. The benzene enhanced, however, the rate so that quantitative conversion of styrene by **1** was obtained in less than 2 h.

1-Methylstyrene reacted very slowly (especially in the presence of **1**) and gave, owing to the steric effect, exclusively the linear aldehyde. Hydroformylation of allyl phenyl ether by **2** yielded, in addition to the linear aldehyde, $PhO(CH_2)_3CHO$ also phenol and 1- and 2-butanal. The amount of the latter product which was only 1% in the first run increased in consecutive runs on account of the main reaction product.

In conclusion, we have demonstrated the potential utility of sol–gel catalyst encapsulation methodology in a variety of organic reactions. While covalent entrapment is a fairly known process [13], we could show that the simpler direct physical caging is at least as efficient and useful for heterogenizing of metal–onium ion-pair catalysts.

Acknowledgements

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