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Homogeneous and alumina supported rhodium complex catalyzed hydrogenation

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Abstract

The complex $Rh(OH)(CO)(PPh_3)_2$ in homogeneous as well as in γ-Al_2O_3 supported system was used as catalyst precursor for hex-1-ene and benzene hydrogenation at 80°C and 6.5 atm of H_2. The hydride complexes, $HRh(CO)(PPh_3)_3$ and $HRh(CO)(PPh_3)$, identified by ^1H and ^{31}P NMR studies, were found to be the active forms in the homogeneous system. γ-Al_2O_3 supported $Rh(OH)(CO)(PPh_3)_2$ complex, activated for 2 h in hydrogen atmosphere does not change its catalytic activity for four weeks. X-ray diffraction spectra show that hydrogenation proceeds with participation of rhodium complexes rather than rhodium metal catalytic centers.

Key words: alumina; hydrogenation; NMR spectroscopy; rhodium

Introduction

Rhodium complexes are well known as very active homogeneous catalysts of many reactions like hydroformylation, isomerization and hydrogenation [1, 2].

Studies on the hydrogenation of olefins show especially high activity for the following complexes: $RhCl(PPh_3)_3$ [3], $HRh(CO)(PPh_3)_3$ [4] and others with polydendate phosphines [5–9]. $Rh(acac)\{P(OPh)_3\}_2$ catalyzes hydrogenation of terminal olefins as well as aromatic ring containing compounds [10]. It is well documented that in all cases the catalytically active form is rhodium hydride complex [1, 11–13].

Here we present the results of our studies on activity of $Rh(OH)(CO)(PPh_3)_2$, the catalyst precursor, in hydrogenation of unsaturated and aromatic compounds (hex-1-ene, benzene) in homo- and heterogenized systems.

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$Rh(OH)(CO)(PPh_3)_2$ was selected as catalyst precursor for two reasons. First, it was expected that the presence of the rather labile OH ligand in the coordination sphere could facilitate the formation of the catalytically active species. Secondly, it was known that OH ligand may also be used for bonding to the alumina (γ-Al_2O_3).

Results and discussion

Homogeneous hydrogenation of hex-1-ene

$Rh(OH)(CO)(PPh_3)_2$ complex is quite a good catalyst precursor for the homogeneous hydrogenation of hex-1-ene and benzene in relatively mild conditions (80°C, 6.5 atm H_2) (Table 1). In one hour, one mole of catalyst hydrogenizes ca. 2000 moles of hex-1-ene and ca. 300 moles of benzene respectively. As predicted for when benzene was used as a solvent for hex-1-ene, only traces of cyclohexane were detected whereas hex-1-ene was totally converted to hexane. Rhodium catalyst precursor can be modified with excess of phosphine, however its activity unexpectedly decreases (Table 1).

The reactive form of the catalyst is relatively stable or easily reproduced during reaction-product separation, therefore the catalyst can be used several times.

TABLE 1

Hydrogenation of hex-1-ene and benzene with $Rh(OH)(CO)(PPh_3)_2$ and $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$ in homogeneous system $[Rh]=8.6\times10^{-6}$ mol in benzene (0.5 cm^3) 80°C, 6.5 atm H_2)

No.	[hex-1-ene] (mol)	time (min)	[hexane] (%)	[hex-2-ene] (%)
1	1.6×10^{-2}	80	100	-
2	8.1×10^{-3}	60	100	
2a[a]	8.1×10^{-3}	30	100	
2b[a]	8.1×10^{-3}	30	100	
3[b]	8.1×10^{-3}	30	80	20
3a[a]	8.1×10^{-3}	40	90	10
	[benzene] (mol)	time (min)	[cyclohexane] (%)	TON (m^{-1} h^{-1})
4	1.7×10^{-2}	140	25	204
5	2.26×10^{-2}	90	16	300
6	2.26×10^{-2}	60	11	300
7[c]	1.7×10^{-2}	100	37	420

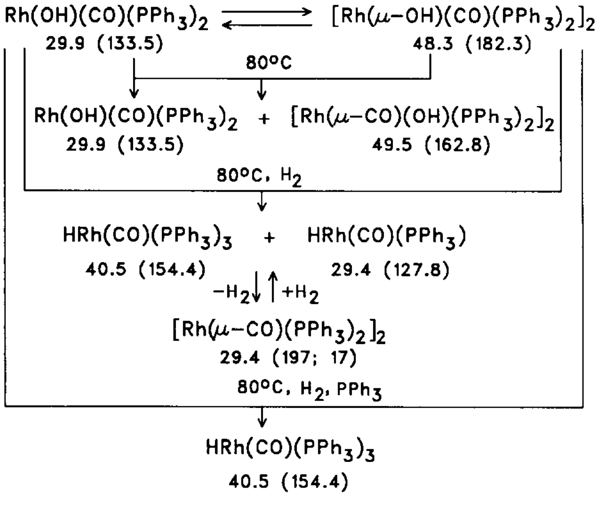
[a] Hex-1-ene was added after separation of the reaction products under vacuum, at room temperature.
[b] Reaction with 4.2×10^{-5} mol of PPh_3 added.
[c] Catalyst: $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$.

The post-distillation residue is benzene-soluble, which means that metallic rhodium forms are not present in the system. However, the Rh(0) complex, $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$ was identified and isolated in solid from the reaction mixture. Its catalytic activity in hydrogenation of benzene is similar or even higher than that of starting complex $Rh(OH)(CO)(PPh_3)_2$ (Table 1).

Spectroscopic studies of the catalytic system

A ^{31}P NMR spectrum of good quality could not be well recorded for $Rh(OH)(CO)(PPh_3)_2$ because of its poor solubility in benzene or toluene. It shows two sets of broad signals at $\delta = 30$ and 50 ppm respectively. A better spectrum was obtained in chloroform where a rather weak doublet at 48.3 ppm (J(Rh–P) 182.3 Hz and very strong doublet at 29.8 ppm (J(Rh–P) 133.5 Hz), assigned to the starting complex $Rh(OH)(CO)(PPh_3)_2$, were observed (^{31}P NMR spectrum of $Rh(OH)(CO)(PPh)_3)_2$ in CH_2Cl_2 [14] is the following: 36.5 ppm, J(Rh–P) 138 Hz).

The doublet at 48.3 ppm with relatively high coupling constant J(Rh–P) may suggest partial dimerization of rhodium complex through OH groups (Scheme 1). When heated in benzene in nitrogen atmosphere (1 h at 80°C) all complexes are completely dissolved, and a well resolved doublet in the ^{31}P NMR spectrum ascribed to the monomer, $Rh(OH)(CO)(PPh_3)_2$, is observed. Simultaneously, partial dimerization proceeds during heating, as indicated the appearance of a new doublet at 49.5 ppm (J(Rh–P) 162.8 Hz) and the formula, $[Rh(\mu\text{-}CO)(OH)(PPh_3)_2]_2$, for dimeric complex could be proposed. The IR spectrum of the heated solution (in cyclohexane) shows a very strong band at 1720 cm^{-1} derived from bridging carbonyl groups; (for monomeric $Rh(OH)(CO)(PPh_3)_2$ complex in Nujol, the ν(CO) frequency was found at 1965 cm^{-1}).



Scheme 1.

Alternatively, the rhodium(0) dimeric complex, $[Rh(\mu\text{-}CO)(PPh_3)_2(S)_2]_2$ (S = solvent), was considered. However the ^{31}P NMR of specially prepared $[Rh(\mu\text{-}CO)(PPh_3)_2(EtOH)_2]_2$ complex shows signals in another region (36.6 ppm, $J(Rh\text{–}P)$ 195.8 Hz), therefore we suggest that the complex under discussion is rather the Rh(I) dimer with carbonyl bridges (Scheme 1).

In the hydrogenation reaction conditions (80°C, 6.5 atm H_2, benzene as solvent), $Rh(OH)(CO)(PPh_3)_2$ is converted into a the mixture of three complexes: $HRh(CO)(PPh_3)_3$, $HRh(CO)(PPh_3)$ and $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$. $HRh(CO)(PPh_3)_3$ (^1H NMR −9.1 ppm, m) was found in the solution of $Rh(OH)(CO)(PPh_3)_2$ which had been heated for less than 1 h in H_2 atmosphere. When heated for longer, coordinatively unsaturated species, $HRh(CO)(PPh_3)$ (^{31}P NMR 29.4 ppm, $J(Rh\text{–}P)$ 127.8 Hz; ^1H NMR −8.6 ppm, m) was detected as a main product. The similar extensive phosphine dissociation leading to $HRh(CO)(PPh_3)$ formation was proposed for the rhodium hydrido complexes [15]:

$$HRh(CO)(PPh_3)_3 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} HRh(CO)(PPh_3)_2 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} HRh(CO)(PPh_3)$$

Attempts to obtain $HRh(CO)(PPh_3)_3$ or $HRh(CO)(PPh_3)$ as solids led only to isolation of the dimeric species, $[Rh(\mu\text{-}CO)(PPh_3)_2]_2$, ($^{31}P$ NMR 29.4 ppm, $J(Rh\text{–}P)$ 197 Hz, $^2J(Rh\text{–}P)$ 17 Hz; IR/cm^{-1} $\nu(CO)$ 1965, molecular weight determined in $CHCl_3$ by the osmometric method $M = 1310$, calc. 1310). This complex was earlier described as the reaction product of $[Rh(\mu\text{-}CO)(PPh_3)_2(EtOH)_2]_2$ with H_2 [16].

The results obtained suggest that in hydrogenation reaction condition $Rh(OH)(CO)(PPh_3)_2$ is easily converted into hydride species which are catalytically active. Dihydrogen activation proceeds also in presence of free triphenylphosphine ligand.

$HRh(CO)(PPh_3)_3$ was identified and isolated in solid (IR/cm^{-1} 2040 $\nu(Rh\text{–}H)$, 1920 $\nu(CO)$) from the solution of $Rh(OH)(CO)(PPh_3)_2$ containing excess of PPh_3 after heating in H_2 atmosphere. $HRh(CO)(PPh_3)_3$ was the only product of that reaction, however the presence of $HRh(CO)(PPh_3)_2$ in reaction mixture cannot be excluded. The ^{31}P NMR spectra of $HRh(CO)(PPh_3)_3$ and $HRh(CO)(PPh_3)_2$ are identical. This was proved by comparison of ^{31}P NMR spectrum of $HRh(CO)(PPh_3)_3$ and that of the H_2-saturated solution of $[Rh(\mu\text{-}CO)(PPh_3)_2(EtOH)_2]_2$ complex. The latter dimer [16], reacts with H_2 to give $HRh(CO)(PPh_3)_2$ [16].

Catalytic activity of alumina supported Rh(OH)(CO)(PPh$_3$)$_2$ complex

Catalyst preparation and examination

The $Rh(OH)(CO)(PPh_3)_2$ complex was supported on $\gamma\text{-}Al_2O_3$ pellets by impregnation from a toluene solution. The absorbance measurements of the complex solution at 361 nm (ϵ 3×10^3 $m^{-1}\cdot l\cdot cm^{-1}$) before and after impregnation were used for determination of rhodium complex concentration in heterogenized catalyst. Such prepared pellets were carefully washed with toluene and dried in a vacuum before use. Results of hydrogenation of hex-1-ene with several heterogenized catalysts are collected in Table 2.

Freshly prepared heterogenized rhodium catalyst is practically inactive and the induction period was observed in all reactions. Hex-1-ene hydrogenation and isomerization products (hexane and hex-2-ene respectively) appear after 2–3 h of the reaction course. The induction period in which catalytic activity of the initial form of catalyst appears, does not depend on the rhodium concentration in a pellet. Especially arranged experiments proved that the catalytically active form of the catalyst can be obtained by maintaining freshly prepared heterogenized samples at 80°C in H_2 atmosphere (6.5 atm) during ca. 2 h. The above procedure can be realized in two ways: (i) heating dry pellets (ii) covered with a solvent (benzene or heptane can be used). Heating of the pellets in nitrogen atmosphere does not produce active catalyst. The above observation permits the assumption that in both the heterogeneous and ho-

TABLE 2

Hydrogenation[a] of hex-1-ene and hex-2-ene with $Rh(OH)(CO)(PPh_3)_2/Al_2O_3$ ([hex-1-ene] 4×10^{-3} mol in toluene (2 cm^3) 80°C, 6.5 atm H_2)

1	5×10^{-6}	60	-	-
1a	-	120		
2	1.3×10^{-5}	60	-	-
2a	-	140	44	56
3	2.4×10^{-5}	60	-	10
3a		180	18	13
4	2.8×10^{-5}	60	-	-
4a		120	5	14
4b		210	15	70
4c		180	-	100
5	4.7×10^{-5}	60	-	-
5a		180	-	8
6 (i)	6.3×10^{-5}	60	-	95
7 (ii)	1.8×10^{-5}	60	50	36
8 (iii)	6.3×10^{-6}	60	-	100
9 (iv)	6.3×10^{-6}	60	-	100

[a] For catalyst activation: the pellets were heated during 2 h at 80°C in following conditions: (i) 6.5 atm of H_2 without solvent, [hex-1-ene] 8×10^{-3} mol; (ii) 1.5 atm of N_2 without solvent, [hex-1-ene] 8×10^{-3} mol; (iii) 6.5 atm of H_2 in heptane, [hex-2-ene] 8×10^{-3} mol; (iv) 6.5 atm of H_2 in heptane, 4 h, [hex-2-ene] 8×10^{-3} mol.

[b] For a, b, c, d, the same pellet was used.

TABLE 3

Hydrogenation of hex-1-ene and benzene with $Rh(OH)(CO)(PPh_3)_2/Al_2O_3$ (the same pellet) ([Rh] 1×10^{-5} mol [hex-1-ene] 8×10^{-3} mol in benzene (1 cm^3) 80°C, 6.5 atm H_2)

No.	t (h)	hexane (%)
1	3	32
2	2	88
3	1	98
4	1	97
5	1	95
6	1	100
7	1	98
8[a]	3	11
9[b]	3	10
10[c]	1	100
11[d]	1	7 (9% hex-2-ene)

[a] Hydrogenation of benzene (2.25×10^{-2} mol); product: cyclohexane.
[b] Hydrogenation of toluene (1.41×10^{-2} mol); product: methylocyclohexane.
[c] [hex-1-ene]: 1.6×10^{-2} mol.
[d] Catalyst deactivated by heating (500°C) in oxygen atmosphere.

mogeneous systems, the rhodium hydride complex is responsible for catalytic activity.

The active form of the heterogenized catalyst can be applied both for hex-1-ene and hex-2-ene hydrogenation (Table 2). Repeatedly used pellets for hydrogenation of hex-1-ene, benzene and toluene confirmed the stability of the heterogenized catalyst. The catalyst, tested for dozens of hours, revealed constant activity and strong attachment of complex to the support. Four weeks storage in ambient conditions in oxygen atmosphere did not change the catalytic activity, however, at higher temperature (500°C) the catalyst undergoes deactivation. Such behaviour was demonstrated in experiment when highly active catalyst (heated for 6 h at 80°C in H_2 atmosphere) was next overheated at ca. 500°C in oxygen atmosphere (Table 3, exp. 11d).

Structure of rhodium alumina supported catalyst

Selection of $Rh(OH)(CO)(PPh_3)_2$ for heterogenization was dictated by the assumption that presence of OH group will facilitate attachment to the γ-Al_2O_3 surface. As a matter of fact this complex is easily and strongly bonded to the alumina from its benzene or toluene solutions producing heterogenized catalyst containing rhodium complex practically not elutable with benzene or toluene.

Our attempts to attach another rhodium complex to γ-Al_2O_3 (like $Rh(acac)(CO)_2$) failed. However, when γ-Al_2O_3 surface was first functionalized with $HP(O)(OPh)_2$, its ability to interact with $Rh(acac)(CO)_2$ dissolved in benzene or toluene, increases and the heterogenized catalyst obtained showed

TABLE 4

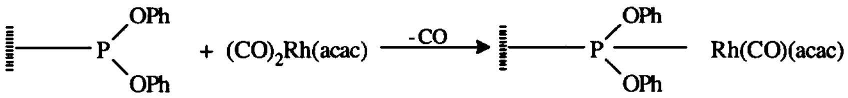
Hydrogenation of hex-1-ene with Rh(acac)$(CO)_2/Al_2O_3$ functionalized with $HP(O)(OPh)_2$ (the same pellet ([Rh] 1.9×10^{-5} mol [hex-1-ene] 8×10^{-3} mol in benzene (1 cm^3) 80°C, 6.5 atm H_2)

No.	t (h)	Reaction products (%)	
		hex-2-ene (%)	hexane (%)
1	3	14	34
2	3	19	39
3	3	21	52
4	2	18	36
5	1	24	13

activity in hex-1-ene hydrogenation (Table 4). It was expected, that diphenylphosphite $HP(O)(OPh)_2$ which exists in two forms according to the possible equilibrium:

$$HP(O)(OPh)_2 \rightleftharpoons P(OH)(OPh)_2$$

will first interact with the γ-Al_2O_3 surface and then permits attachment of Rh(acac)$(CO)_2$ complex via CO substitution:



X-ray diffraction studies of alumina supported Rh(OH)(CO)$(PPh_3)_2$

The diffraction spectra of pure alumina support shows a typical γ-Al_2O_3 phase (Fig. 1(1)). After heterogenization of the Rh(OH)(CO)$(PPh_3)_2$ complex low intensity peaks in the low angle region ($2\theta=7.30°$, 9.66°, 14.00°) were observed (Fig. 1(2)). This kind of spectrum may suggest that γ-Al_2O_3 supported complex exists in a quasi-two-dimensional layer structure.

This structure did not change after calcination of pellets in hydrogen atmosphere (at 80°C, 6.5 atm H_2, during 2 h) or during hydrogenation reaction carried out ca. 8 h. This is proved by the appearance only very low intensity peak at $2\theta=18.00°$ (Fig. 1(3)). The calcination of pellets at 500°C in oxygen atmosphere leads to the drastic decrease of catalytic activity and to a large increase of intensity of the peak at $2\theta=18°$ (Fig. 1(4)). It may suggest that the rhodium atoms arrangement increases in one of the planes but the absorbed layer still has quasi-bi-dimensional character. All of the observed peaks cannot be attributed to crystalline phases of Rh_2O_3, RhO_2 or Rh metal. Rh(OH)(CO)$(PPh_3)_2$ complex used as a catalyst precursor does not undergo reduction to metallic rhodium in either homo- or the heterogenized systems.

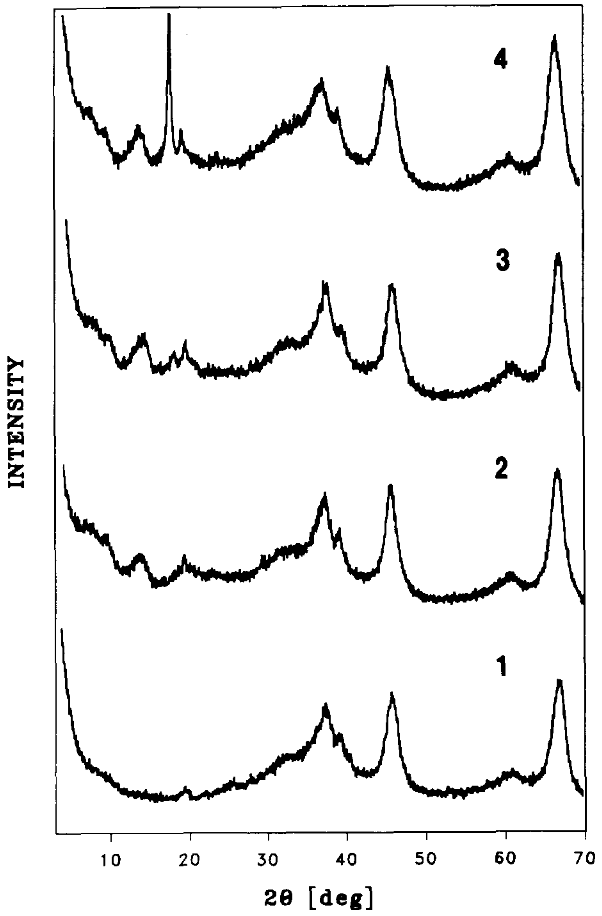


Fig. 1. X-ray powder spectra of (1) alumina carrier; (2) freshly supported Rh(OH)(CO)$(PPh_3)_2$ complex; (3) after use 8 h in H_2 atmosphere; (4) after calcination at 500°C in air.

This permits the conclusion that hydrogenation of unsaturated hydrocarbons is catalyzed by the rhodium complex and not the rhodium metal.

Experimental

The rhodium complexes were prepared by the methods described in the literature: Rh(OH)(CO)$(PPh_3)_2$ [14], HRh(CO)$(PPh_3)_3$ [15], [Rh(μ-CO)$(PPh_3)_2(EtOH)_2]_2$ [15], Rh(acac)$(CO)_2$ [19]. Benzene, hex-1-ene and hex-2-ene were carefully distilled.

The hydrogenation reaction was carried out in thermostated steel autoclave of 40 cm^3 or 200 cm^3 volume. Reagents were introduced into the autoclave in nitrogen atmosphere and then 5 atm of H_2 pressure was applied. After the reaction was complete, the autoclave was cooled and a sample was taken for analysis.

The reaction products were analyzed with ^1H NMR (Tesla BS 567A, 100 MHz spectrometer) and GC–MS (Hewlett-Packard instrument) methods. The NMR spectra (^1H and ^{31}P) were recorded on Bruker 300 spectrometer; the UV–Vis spectra were measured on Specord M-40 and IR spectra on Specord M-80 spectrophotometers.

The pellets of γ-Al_2O_3 were obtained by the wet pressing at 550 MPa of transition alumina powder prepared by flash calcination of gibbsite at 575–600°C [20, 21]. Next, the pellets were rehydrated in water vapour at 20°C during 20 h, and in water at 70°C during 5 h. After such treatment the pellets were dried at 105°C and calcined at 480°C during 3 h. The specific surface area determined with nitrogen by BET method using Perkin Elmer 212 Sorptiometer was 296 m^2/g and the pore volume $V_p = 0.34$ cm^3/g.

The X-ray diffraction measurements were recorded on X-ray Powder Diffractometer DRON-3 (CuK_α and Ni filter).

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