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Highly Chemoselective Reduction of Aldehyde Function Catalyzed by Polymer-Bound Rh_6 Cluster Complex under Water-Gas Shift Reaction Conditions

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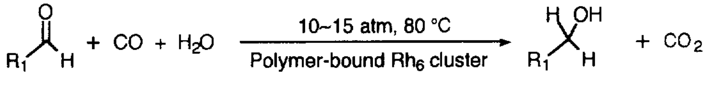
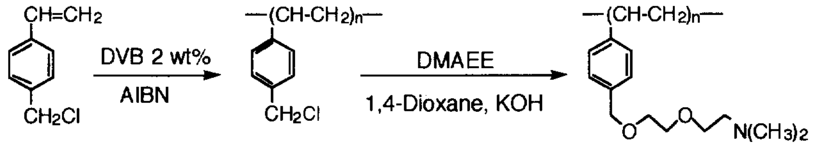
Abstract: A functionalized polymer-bound Rh_6 cluster complex showed high catalytic activity for chemoselective reduction of aldehydes in the presence of CO and H_2O. The reaction system consists of the triphase, which makes work-up procedure simple. © 1997 Elsevier Science Ltd.

Immobilization of metal cluster complexes onto organic or inorganic polymers has been extensively developed for preparation of new type catalysts, which has been expected to show novel catalysis based on interactions between supports and metals.[1] We found that homogeneous catalyst systems consisting of $Rh_6(CO)_{16}$ and amines had high activities for the water-gas shift reaction (WGSR), reduction of aldehydes, and deoxygenation of various N-O bonds under the WGSR conditions.[2] Recently, it is very interesting for organic syntheses to use water as a hydrogen source in place of molecular hydrogen, since water is a safety and cheap material.[3] Using aminated polystyrenes, the above $Rh_6(CO)_{16}$–amine systems could be heterogenized to form polymer-bound Rh cluster complexes.[4] Selective reduction of one carbonyl group in the presence of other functional groups is a fundamental process in organic syntheses. Here, we wish to report the highly chemoselective reduction of aldehyde function catalyzed by a polymer-bound Rh_6 cluster complex (Eq. 1). The above catalytic reduction can be achieved by some of metal hydrides and hydrogen transfer reagents as stoichiometric material.[5] To our knowledge, few examples of the selective reduction of aldehyde using catalysts were reported.[6]



$$R_1CHO + CO + H_2O \xrightarrow[\text{Polymer-bound } Rh_6 \text{ cluster}]{10\sim15 \text{ atm, } 80\ ^\circ C} R_1CH_2OH + CO_2 \qquad (1)$$

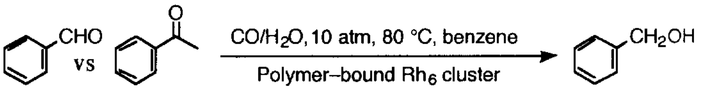
We have already reported that a catalyst system of $Rh_6(CO)_{16}$ and *N,N,N',N'* –tetramethyl–1,3–propanediamine chemoselectively reduced aldehyde function in α,β–unsaturated aldehydes using CO and H_2O as a reducing agent, where 2-ethoxyethanol was a good solvent. In order to heterogenize the Rh catalyst, the amine additive, and the solvent, a multifunctionalized polystyrene having 2-(dimethylamino)ethoxy moieties was synthesized according to the modified literature procedure.[7] Bulk polymerization of *p*-(chloromethyl)styrene and divinylbenzene (98/2, w/w) was carried out using AIBN, followed by amination with (2-(dimethylamino)-ethoxy)ethanol (DMAEE) (Eq. 2). The obtained amino-substituted polymer displayed a 90 % degree of the amination of chloromethyl moieties (Anal. Found: C, 78.77; H, 9.01; N, 5.70; Cl, < 0.03).



(2)

Reduction of 1-naphthaldehyde was carried out as a typical example. A stainless steel autoclave containing $Rh_6(CO)_{16}$ (0.010 mmol) and the aminated polymer (40 mg, 0.18 mmol of N) was evacuated and flushed three times with CO. A benzene (3.0 mL) solution of the substrate (1.5 mmol) and H_2O (80 mmol) were added successively. The reaction mixture was stirred at 80 °C under 15 atm of CO. After 24 h, brownish violet solid was filtered (IR: 2075 w (sh), 2066 w, 2035 s, 1992 s (br), 1970 s (br), 1803 w (sh), 1769 s (br) cm^{-1}; Nujol mull).[8] The filtrate was then extracted with ether, followed by concentration, and the residue was subjected to short-path column chromatography on silica gel with a 10:1 mixture of n-hexane and ethyl acetate, which gave 1-naphthalenemethanol (0.200 g, 85 %). ^1H NMR ($CDCl_3$, 270 MHz): δ 1.73 (s, 1H, OH), 5.12 (s, 2H, CH_2), 7.39-7.56 (m, 4H), 7.78-8.12 (m, 3H). M.p. 64.0 °C.[9]

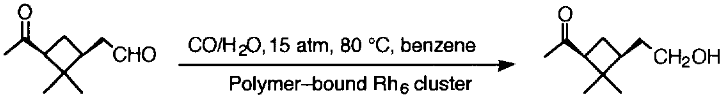
Results of the reduction of various aldehydes using $Rh_6(CO)_{16}$ and the aminated polymer are shown in Table 1 with those of the comparative homogeneous system using triethylamine. Many aromatic aldehydes were reduced to corresponding alcohols in high yields under 10~15 atm of CO in benzene solvent at 80 °C. Generally, introduction of substituents into the *para* position of benzaldehyde retarded the reduction rate. In the case of aliphatic aldehydes, corresponding alcohols were also obtained, but 1-octanal and 2-ethylbutanal showed relatively low reactivities (Runs 12 and 13). An intermolecular competitive reduction of benzaldehyde and acetophenone gave only benzyl alcohol without formation of 1-phenylethanol from acetophenone (Eq. 3).



(95 %)

(3)

High chemoselectivity of the polymer-bound Rh_6 cluster catalyst could be also confirmed by the following intramolecular competitive reduction; *cis* -3-acetyl-2,2-dimethylcyclobutaneacetaldehyde[10] **1** gave exclusively *cis* -3-acetyl-2,2-dimethylcyclobutaneethanol[11] **2** in 90 % yield (83 % isolated) without products from reduction of the ketone group (Eq. 4).



1

2 (83 %)

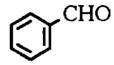
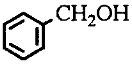
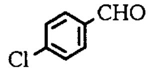
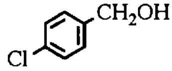
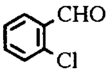
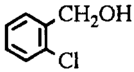
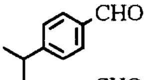
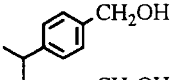
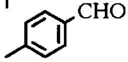
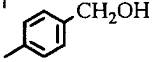
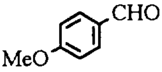
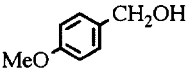
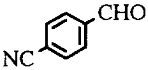
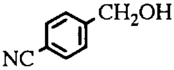
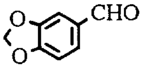
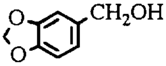
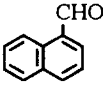
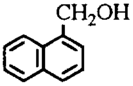
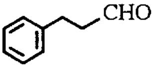
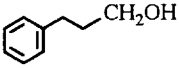
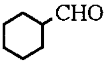
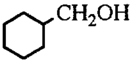
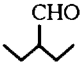
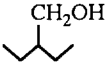
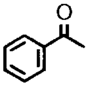
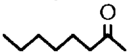
(4)

After the reduction of benzaldehyde, the polymer-bound Rh catalyst was recovered by filtration and washed with benzene for three times. The recovered polymeric Rh catalyst gave 93 % yield of benzyl alcohol without appreciable loss of its activity under the same conditions as in the case of a fresh catalyst.

A corresponding homogeneous Rh system using triethylamine in place of the aminated polystyrene showed lower activity for aldehyde reductions than the heterogeneous polymeric system using the same concentration of amine moieties, which might be due to effect of ligand concentration in polymer matrix.

We think that an active species in the above reduction is $[Rh_6(CO)_{15}H]^-$. The hydride Rh cluster anion

Table 1. Reduction of Various Aldehydes and Ketones in the Presence of CO and H_2O [a]

Run	Substrate	Product	Pco (atm)	Yields (%)[b]	
				Hetero.[c]	Homo.[d]
1			10	96 (82)	22
2			15	93 (86)	12
3			10	97 (87)	22
4			15	98 (87)	4
5			15	93 (87)	9
6			15	91 (83)	14
7			15	93 (89)	19
8			15	98 (83)	16
9			15	95 (85)	20
10			10	89 (82)	26
11			15	99 (91)	30
12			10	27	22
13			10	43	9
14		no reaction	10	0	0
15			10	trace	0

[a] Reaction conditions: substrate 1.5 mmol, $Rh_6(CO)_{16}$ 0.01 mmol, benzene 3.0 ml, H_2O 80 mmol, the aminated polymer 40 mg (0.18 mmol of N), 80 °C, 24 h. [b] Yields were determined by GC using internal standard technique.[c] Values in parentheses are isolated yields. In isolation of products, use of column chromatography on silica gel (Wako Gel C-200) with a 10:1 mixture of n-hexane and ethyl acetate gave pure reduction products. [d] Values are for the corresponding homogeneous system: NEt_3 0.18 mmol, H_2O 40 mmol, 1,4-dioxane 3.0 ml, 80 °C, 24 h.

$[Rh_6(CO)_{15}H]^-$ was detected under the WGSR conditions; the Rh cluster anion derived from nucleophilic attack of OH^- on $Rh_6(CO)_{16}$ is bound to the aminated polystyrene through ionic bonding with ammonium cation in the polymer.[12] The same Rh species could be also generated in the aminated polystyrene using CO and H_2, which showed high chemoselectivity for the aldehyde reduction.[7b]

In conclusions, the polymer-bound Rh cluster complex has high chemoselectivity for the reduction of aldehyde function under the WGSR conditions. Use of the present polymeric Rh reagent forms triphase system of aqueous, organic phase, and polymer solid,[13] which leads to easy separation of both catalyst and products from the reaction mixture. Furthermore, the above heterogenization makes the homogeneous Rh catalyst sysytem possible not only to reuse the catalyst, but also to enhance its activity.

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8. The IR spectra of the obtained polymer-bound Rh complexes show formation of $[Rh_{12}(CO)_{30}]^{2-}$ as a main species, which was derived from dimerization of $[Rh_6(CO)_{15}H]^-$. See ref. 7(b). IR assignments: $[Rh_{12}(CO)_{30}]^{2-}$, 2075, 2035, 1803, 1769 cm^{-1}; $[Rh_6(CO)_{15}H]^-$, 2066 cm^{-1}.
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