Liquid Polymer Catalyst Immobilized on Polymer-coated Silica: Application to Hydroformylation

Liang Hong and Eli Ruckenstein*

Department of Chemical Engineering, State University of New York at Buffalo, Box 60, Buffalo, New York 14260-4200, USA

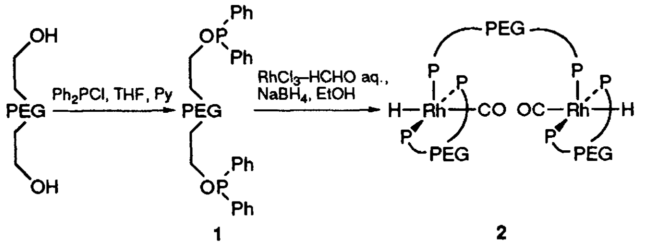
α,ω-Bis(diphenylphosphino)-poly(ethylene glycol-400) and its rhodium carbonyl complex have been attached to a poly(2-hydroxyethyl methacrylate) network coating on porous silica; the supported catalytic liquid polymer phase thus obtained has been used in the hydroformylation of ethyl undec-10-enoate.

A recent paper[1] reports the deposition of polymer chains of quaternary onium salts on the surface of hydrophilic silica by the polymerization of water-soluble quaternary onium monomers present in a water medium that is absorbed by the porous silica. This polymer covered silica surface, to which a small amount of water was added, constitutes a suitable catalytic substrate since it provides cation anchors for negatively charged catalytic species. It was employed by us to immobilize monosulfonated triphenylphosphine and its rhodium carbonyl complex. This system was used for the hydroformylation of ethyl undec-10-enoate, using cyclohexane as the reaction medium. The reaction rate was, however, relatively low because this high molecular mass olefin has a low solubility in the supported aqueous phase. For this reason, a different kind of supported catalyst, namely a liquid polymer, has been attached to a silica surface coated with a suitable polymer network. Because of a higher compatibility of the high molecular mass olefin with the liquid polymer phase a higher reaction rate is expected.

Poly(ethylene glycols) (PEGs) or the macrocyclic crowns derived from them have been widely used as encapsulating hosts for various metal ions in phase-transfer catalysis and extraction processes.[2] It will be demonstrated here that the macrocyclic-crown analogues obtained by substituting the hydrogen or the hydroxy substituents at the ends (α,ω-positions) of the PEG with phosphine groups, and then coordinating the two ends to transition metal atoms constitute a supramolecular catalytic system. The main advantage of such a system is that it can be easily immobilized by anchoring the polyether chains to a substrate, either by hydrogen bonding or coordinative complexing, thus generating a catalytic liquid polyether layer. For this purpose we selected silica particles covered with a poly(2-hydroxyethyl methacrylate) network, to which the phosphino-polyether chains had been attached *via* the hydrogen bonding of the OH groups of the network with the glycol ether units of the latter chains. Compared to the supported aqueous phase catalytic systems,[1] the supported liquid polyether layer is generally more compatible with high molecular mass organic compounds because of its suitable polarity.

The polyether ligand α,ω-bis(diphenylphosphino)poly(ethylene glycol-400) (**1**, Scheme 1) was prepared starting from PEG-400 ($\bar{M}_w$ 400, Aldrich). Diphenylphosphinous chloride (23 g, 100 mmol) in tetrahydrofuran (THF) (20 ml) was dropped into a stirred solution of PEG-400 (20 g, 50 mmol) and pyridine (Py) (8.0 g, 100 mmol) in THF (30 ml) at room temperature. The reaction mixture was stirred for 3 h, then the precipitated Py·HCl was filtered out. The THF solution was passed through a silica-gel column to remove the dissolved Py·HCl. After the solvent THF had been evaporated off, 32 g of α,ω-bis(diphenylphosphino)-PEG-400 **1** was obtained. The molecular mass distribution of **1** was determined by fast atom bombardment (FAB) mass spectrometry. The yellow–green rhodium carbonyl complex (Wilkinson type complex) was prepared by the conventional method.[3] Elemental analyses indicated P : Rh = 3 : 1; FTIR: ν(Rh–H) 2171 cm^{-1} and ν(CO) = 2004 cm^{-1}; the ^{31}P NMR signals changed from δ 19.5 (t) and 22.5 (t) before coordination to δ 80.14 (m) and 80.92 (m) after coordination. The structure of this complex is not yet clear. It may have the structure **2** in Scheme 1, but other possibilities include a coordinative polymeric structure involving successive PEG bridges. Structure **2** seems to be most likely because the complex can be easily dissolved in THF without a major change in viscosity. In addition, Alcock *et al.*[4] have determined by X-ray diffraction a similar structure for phosphino-ether carbonyl complexes which had, however, a shorter PEG chain than ours. Since both the bisphosphino-PEG ligand **1** and the Wilkinson complex **2** have low solubilities in non-polar solvents, it is possible to support them (as a solution of **2** in **1**) on a substrate in order to catalyse organic conversions in which the reactants and products are soluble in non-polar media. The immobilization of the catalytic species is hence a result of their hydrogen bonding to the polymer coated silica and of their insolubility in the non-polar reaction medium.

In this paper, a hydrophilic silica powder (600 m^2 g^{-1}; pore volume 1.1 ml g^{-1}; average particle size 10 μm; Aldrich) was selected as the substrate. To increase the compatibility between the substrate and the immobilized liquid polymer,



PEG = –[OCH$_2$CH$_2$]$_n$–; P in complex **2** is OP(Ph)$_2$

n = 6 (19.5%), 7 (18.2%), 8 (29.8%), 9 (22.1%), 10 (10.4%)

Scheme 1 Synthesis of polyether phosphine ligand **1** and of its Wilkinson complex **2**

Table 1 Hydroformylation of ethyl undec-10-enoate during six reuses of the same supported liquid polyether catalyst[a]

Run	Reaction time/h (*i*)	Reaction time/h (*ii*)	Total yield of aldehydes **3** and **4** (%)[b] (*i*)	Total yield of aldehydes **3** and **4** (%)[b] (*ii*)	3/4 for (*i*)
1	2.0	2.5	67	34	1.0
2	2.0	2.5	64	35	1.2
3	2.5	2.5	60	33	1.3
4	2.5	2.5	55	34	1.6
5	4.0	5.0	48	45	1.8
6	4.0	5.0	42	43	2.0

[a] Conditions: 800 psi CO–H$_2$ (1 : 1); 85 °C; olefin, 15 g (71 mmol); reaction medium (cyclohexane), 40 ml. Molar ratio olefin/Rh *ca.* 1000. The supported-catalyst system (*i*) contained 0.5 g of substrate and (*ii*) 2.0 g of substrate. [b] The aldehydes were separated from the unreacted olefin by silica-gel column chromatography, using gradient elution with light petroleum–diethyl ether.

poly(hydroxyethyl methacrylate) crosslinked with *N,N*-methylene bisacrylamide (MBAA) was first deposited on silica, by the radical polymerization of the water-soluble monomers 2-hydroxyethyl methacrylate (HEMA) and MBAA present in a water medium that is absorbed by the pores of the silica particles. After polymerization, the coated substrate was washed with THF by Soxhlet extraction in order to remove the unreacted monomers. Elemental analyses indicated that the polymer-coated substrate contained 2.72 mmol of HEMA and 0.34 mmol of MBAA per gram of substrate. The supported liquid polyether catalyst was obtained by the reaction of $RhCl_3 \cdot 3H_2O$ (0.02 g, 0.075 mmol) with an excess of **1** (0.72 g, 1 mmol, calculated from the average molecular mass) in ethanol (15 ml), and then introducing the polymer-coated silica powder (either 0.5 g or 2.0 g) into the ethanol solution. The ethanol solvent was evaporated *in vacuo* with magnetic stirring, and the liquid polymer remained deposited on the PHEMA network coating the silica particles.

In order to examine the hydroformylation of a high molecular mass olefin by this supported catalyst, ethyl undec-10-enoate was selected [eqn. (1)]. Table 1 lists the

$$RCH{=}CH_2 + CO + H_2 \rightarrow \underset{\mathbf{3}}{RCH_2CH_2CHO} + \underset{\mathbf{4}}{RCH(CHO)Me} \qquad (1)$$

$$R = EtO_2C[CH_2]_8$$

yields for this reaction for six successive uses of the same catalytic system. The reaction mixture was easily removed by suction from the supported catalytic powder remaining at the bottom of the pressure reactor. Two kinds of catalysts, (*i*) and (*ii*), were used, which had the same amount of catalytic species but were loaded with different amounts of substrate. For comparison, we note that the supported aqueous catalyst previously used by us[1] to catalyse the hydroformylation of ethyl undec-10-enoate (dissolved in cyclohexane containing some ethanol) provided a 40% yield of aldehyde after 15 h of reaction. Higher hydroformylation rates were achieved with the supported liquid polyether catalyst system employed here, because ethyl undec-10-enoate is much less soluble in the former aqueous than in the present liquid polyether layer. Table 1 also shows that catalyst system (*i*) leads to a higher initial reaction rate than (*ii*), and that the yield of the aldehydes decreases for (*i*) during six successive hydroformylations, but remains almost the same for (*ii*). The mass of the recovered supported-catalyst powder was, after washing with cyclohexane, 70% of its original value after the six reuses in case (*i*), but catalyst (*ii*) was recovered almost completely. It is likely that the generation of aldehydes increases the polarity of the solution, thus promoting the dissolution of the liquid polyether molecules that are not bound sufficiently strongly to the (PHEMA–MBAA) network. Larger amounts of substrate are likely to increase the strength of the binding of the catalytic species to the substrate. This explains why in case (*ii*) the recovery of supported-catalyst after six reuses was almost complete. From the 70% recovery after a total of 17 h of reaction for catalyst (*i*), one can estimate that 1 g of substrate possesses a maximum accommodation capacity of about 0.6 g of polyether ligand **1** and its rhodium complex **2**. For the unsupported catalyst under similar conditions after reaction for 5 h, the yield of aldehydes was 47%. The unsupported catalyst is insoluble in cyclohexane, and so was first dissolved in 6 ml of THF. The yields for heterogeneous conditions are thus comparable to those for homogeneous conditions.

Received, 24th May 1993; Com. 3/02967K

References

1 L. Hong and E. Ruckenstein, *J. Catal.*, 1993, **143**, 52.
2 E. Weber, J. L. Toner, I. Goldberg, F. Vögtle, D. A. Laidler, J. F. Stoddart, R. A. Bartsch and C. L. Liotta, *Crown Ethers and Analogs*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1989.
3 D. Evans, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 1968, 2660.
4 N. W. Alcock, J. M. Brown and J. C. Jeffery, *J. Chem. Soc., Chem. Commun.*, 1974, 829.