CATALYTIC VAPOR PHASE HYDROFORMYLATION OF OLEFINS
OVER POLYMER-IMMOBILIZED RHODIUM COMPLEXES

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The rhodium complex ($-RhCl(CO)_2$) coordinatively bonded to the phosphine group on polystyrene coated over silica gel is an efficient catalyst for hydroformylation of olefins at 100°C at 1 atm in vapor phase. The rate expression of propionaldehyde formation was $R = k[H_2][C_2H_4][CO]^{-0.5}$.

It is generally known that rhodium hydrido carbonyl phosphine complexes are highly active and promote the conversion of olefins to aldehydes under very mild reaction conditions.[1,2] These hydroformylation mechanisms were discussed in detail. However, the primary disadvantage of homogeneous catalysts is in the separation of the soluble catalyst and solvent from the reaction products. In the heterogeneous catalysis, on the other hand, this problem is eliminated since the catalyst remains in the solid phase while the reacting gases and products pass over it. However, it is too complicated to investigate the reaction mechanisms, particularly the relation between the chemical structure of the heterogeneous catalysts and the catalytic activity. Transition metal compounds, which are chemically bound to organic polymers through coordination, can exhibit activities identical to those of analogous soluble compounds.[3-9] Recently, new hydroformylation catalysts of polymer-supported rhodium complexes have been reported. However, only products and their distribution were studied in these reaction systems being operated at high pressures in liquid phase.[10-12]

Here we made rhodium-phosphine polymer(polystyrene cross-linked by divinylbenzene) coated over silica gel, since silica gel has no active site for hydroformylation and is able to spread the polymer over its high surface area. This catalyst promotes hydroformylation under atmospheric pressure at 100°C in vapor phase.

For comparison, four kinds of catalysts were prepared in granular form for use in a fixed bed flow reactor. (1) Polymer-immobilized rhodium complex catalyst A and B. The copolymer(Catalyst A: emulsion polymerization; Catalyst B: solution polymerization) of styrene and divinylbenzene were made in the presence of silica gel ($293 \ m^2/g$) to coat over it. The polymer was brominated by using bromine and iron catalyst.[13] A reaction of the brominated copolymer with THF solution of potassium diphenylphosphide yielded polymeric ligand [I]. Treatment of benzene solution of $Rh_2(CO)_4Cl_2$, which was made from $RhCl_3 \cdot 3H_2O$ and carbon monoxide,[14] with polymer [I]   afforded substance [II],

[I]   [II]
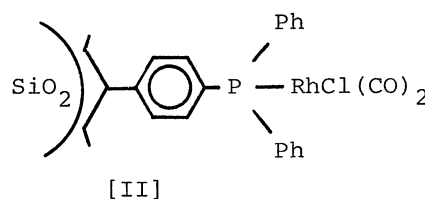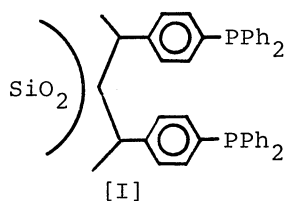
which contained rhodium fixed via Rh-P coordination to the polymer.[15] The BET surface area (N_2 adsorption) of Catalyst A (Rh 8.2 wt%) was 42 m^2/g and that of Catalyst B (Rh 6.5 wt%) was 9.8 m^2/g. The infrared spectra of these catalysts showed two absorption bands (νco) at 2080 and 2020 cm^{-1} for Catalyst A and at 2075 and 1995 cm^{-1} for Catalyst B. In the preparation of rhodium phosphine polymer complexes from $Rh_2(CO)_4Cl_2$, infrared results suggested the formation of a cis-$Rh(CO)_2(PPh_3)Cl$ species within the polymer. The interpretation of the spectra is also considered to be consistent with Rh containing one phosphine and two carbon monoxide ligands.[16] (2) $RhCl(CO)(PPh_3)_2$ on silica gel (Rh 10.3 wt%). Both $Rh_2(CO)_4Cl_2$ and PPh_3 were dissolved in benzene under reflux for 3 hr to give $RhCl(CO)(PPh_3)_2$ and the compound was mixed with silica gel in benzene. The mixture was stirred in benzene for 2 hr and evacuated at room temperature to remove the solvent. (3) $RhCl_3$ on silica gel (Rh 7.9 wt%). $RhCl_3 \cdot 3H_2O$ was dissolved in water and mixed with silica gel and evacuated at 150°C for 4 hr. (4) Rh on silica gel (Rh 9.0 wt%). $RhCl_3$ on silica gel, which was prepared as described above, was reduced by hydrogen stream at 300°C for 4 hr to give Rh on silica gel.

Experiments were performed in a 50 cm pyrex glass tubular reactor, 18 mm in diameter. The reactor held a catalyst charge of 1.6 ml and was positioned vertically in an electric furnace. The reactor was usually loaded with 1.0 g of catalyst and 2 mm pyrex glass beads were packed above and below the catalyst bed. The gaseous reactants, olefin (ethylene or propylene), hydrogen, and carbon monoxide were supplied from the respective cylinder. After being measured separately, the reactants were mixed with each other and were pre-heated at the upper part of the reactor. The hydroformylation reactions were normally performed at 100°C. All the experiments were made under atmospheric pressure. W/F was between 5 and 17 g-cat.hr/mol, where W is the catalyst weight(g) and F is the total gas flow rate(mol/hr). The gaseous product exited from the bottom of the reactor where it was cooled using a small water condenser. The condensed aldehyde product was periodically collected in a glass flask containing water and analyzed by gas chromatography, using 3 m PEG 1500 column at 110°C.

The hydroformylation of ethylene to propionaldehyde with the polymer-immobilized rhodium complexes can be expressed by eq. (1).

$$H_2C=CH_2 + H_2 + CO \longrightarrow CH_3CH_2CHO \qquad (1)$$
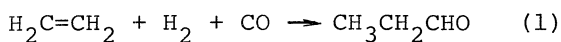
As shown in Fig.1, Catalyst A and B exceptionally promoted the conversion of ethylene to propionalydehyde under mild conditions. The difference of activities between Catalyst A and B may be attributed to the surface area. In order to compare the catalyst activities, $RhCl(CO)(PPh_3)_2$ on silica
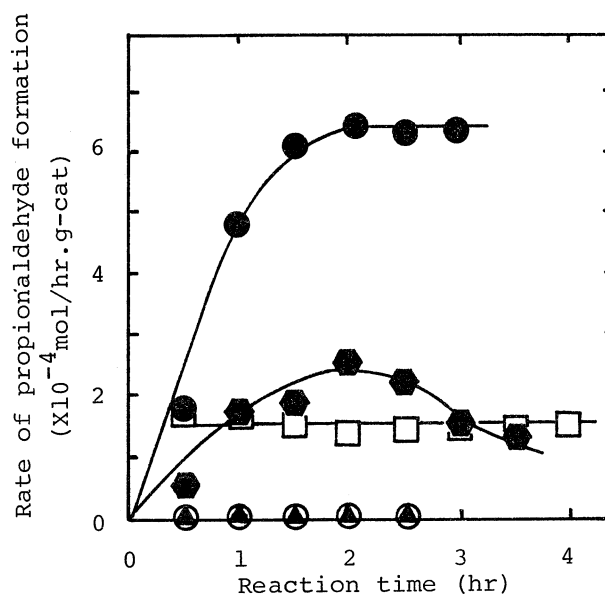

Fig.1. Hydroformylation with various catalysts. Temperature 100°C; Total pressure 1 atm (feed ratio C_2H_4:CO :H_2=1:2:2).
●:Catalyst A. □:Catalyst B. ○:Rh on SiO_2.
▲:$RhCl(CO)(PPh_3)_2$ on SiO_2. ◕:$RhCl_3$ on SiO_2.

gel, $RhCl_3$ on silica gel, and Rh on silica gel were attempted under the same conditions. These catalysts are far less active in hydroformylation. Details of experiments are given in Fig.1. Usually W/F is 5 g-cat.hr/mol, except that W/F of $RhCl(CO)(PPh_3)_2$ on silica gel is 2.5 g-cat.hr/mol. Both Rh metal and $RhCl(CO)(PPh_3)_2$ supported on silica gel exhibited no activity. Propionaldehyde was obtained with $RhCl_3$ on silica gel. Initially the activity increased with reaction time until 2 hr, and then decreased as shown in Fig.1. When the reactor was taken out of the furnace, it was found that a red solid compound adhered on the surface of glass beads below the catalyst bed of the $RhCl_3$ on silica gel. $Rh_2Cl_2(CO)_4$ (red solid compound), which is active in hydroformylation, was formed at the initial stage and was removed from the silica gel surface, therefore the activity fell down. After 2 hr, no noticeable change in conversion was detected up to 20 hr with Catalyst A and B. These results demonstrated that Catalyst A and B had very stable properties due to linking the active species chemically to the surface of a solid support. The ratio of the normal to isobutyraldehyde on propylene hydroformylation was 1.7 for Catalyst B. More normal aldehyde from the hydroformylation of olefins was produced in homogeneous systems.[1,2,17]

Contact time (W/F) was varied from 6 to 17 g-cat.hr/mol by adjusting total flow rate at the base feed composition (C_2H_4:H_2:CO=1:2:2). The effect of contact time on the yield of propionaldehyde with Catalyst B is shown in Fig.2. As one would expect, the yield increased with contact time. In Fig.3, the rates of propionaldehyde formation were measured at 100°C over Catalyst B with varying partial pressures of ethylene, carbon monoxide, and hydrogen with nitrogen as the diluent. The rate equation for propionaldehyde from ethylene, hydrogen, and carbon monoxide was given as
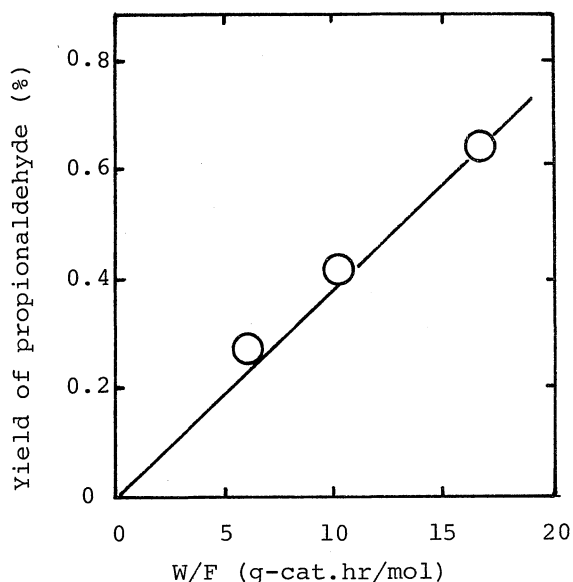

Fig.2. Ethylene conversion versus contact time over Catalyst B. Temperature 100°C; Total pressure 1 atm (feed ratio C_2H_4: CO :H_2=1:2:2).
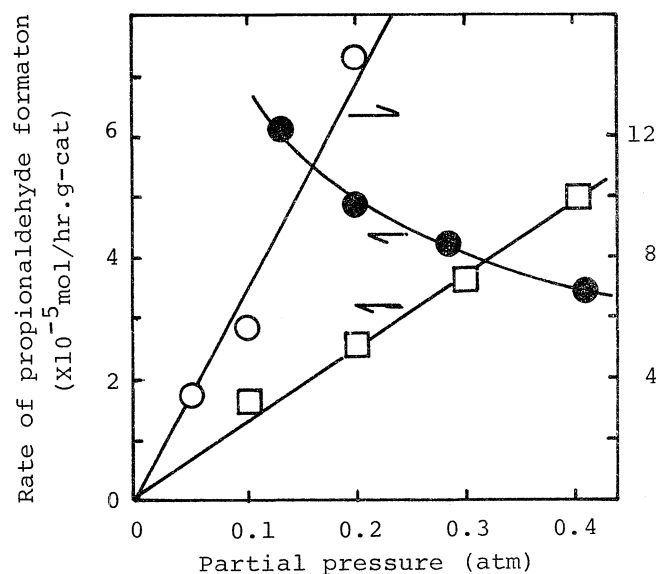
Fig.3. Plot of rate of ethylene hydroformylation over Catalyst B at 100°C, W/F 10 g-cat.hr/mol, and 1 atm total gas pressure against each partial pressure. □:H_2, ○:C_2H_4, ●:CO, the pressure being made up with N_2.

$R = k[H_2][C_2H_4][CO]^{-0.5}$, where $k = 4 \times 10^{-4}$ mol/(hr g-cat.atm$^{3/2}$). For the homogeneous reaction with the RhHCO(PPh$_3$)$_3$ catalyst,[2] the plots of rates against the olefin concentration and hydrogen pressure were linear. There was a strong inhibition by carbon monoxide for hydroformylation, using the RhHCO(PPh$_3$)$_3$ catalyst in benzene. The kinetics of the heptene hydroformylation was studied with the Rh$_4$(CO)$_{12}$ catalyst in hexane.[18] The rate expression for the octanal formation was rate = k[Heptene][Rh][CO]$^{-1}$. The results of the first order dependence on olefin and hydrogen and a strong inhibition by carbon monoxide in the homogeneous reaction of both studies[2,18] agree with those of this kinetic study. These facts will exhibit that a rhodium complex, when confined to the surface of a solid through coordination can act as a catalyst with the same reaction mechanisms as those of catalyst composed of analogous rhodium complexes which are freely soluble.

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