

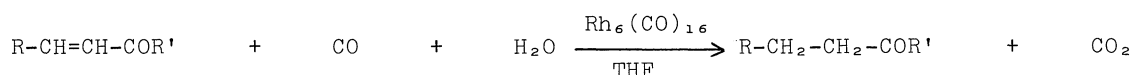
SELECTIVE HYDROGENATION OF α,β -UNSATURATED CARBONYL AND NITRILE COMPOUNDS
CATALYZED BY RESIN-SUPPORTED RHODIUM CARBONYL COMPLEXES

Takanori KITAMURA, Takashi JOH, and Nobue HAGIHARA
The Institute of Scientific and Industrial Research,
Osaka University, Yamada-kami, Suita, Osaka 565

The rhodium carbonyl complexes supported on cross-linked polymeric amines catalyze the heterogeneous hydrogenation of α,β -unsaturated carbonyl and nitrile compounds with carbon monoxide and water.

In recent years several attempts have been made to convert the homogeneous catalysts to heterogeneous ones by the use of polymeric ligands or polymeric supports.^{1,2)} These treatments produce a new class of catalysts having both of the advantages of homogeneous and heterogeneous catalysts.

In the previous paper,³⁾ we reported a convenient method for the selective hydrogenation of α,β -unsaturated carbonyl and nitrile compounds with carbon monoxide and water using rhodium carbonyl as catalyst.



We found that the rate of hydrogenation was increased in the presence of various amines and treatment of polymeric amines such as Amberlyst A-21 or Amberlite IRA-93 (Rohm and Haas) with rhodium complexes afforded the resin-supported catalysts. We wish to report here the selective hydrogenation of α,β -unsaturated carbonyl and nitrile compounds with carbon monoxide and water using polymeric amine-supported rhodium carbonyl catalysts.

The polymeric amine-supported catalyst was prepared as follows. $\text{Rh}_4(\text{CO})_{12}$ (0.031 mmol), Amberlyst A-21 (5 ml, 7 mg equiv. as N,N-dimethylbenzylamine group), H_2O (0.15 ml) and tetrahydrofuran (15 ml) were weighed into a glass tube placed in a 100 ml stainless steel autoclave. It was then pressurized with 100 kg/cm² of carbon monoxide. After heating at 100°C for 5 hr, the autoclave was cooled and depressurized to give red colored resin particles suspended in red solution. When the carbon monoxide atmosphere was replaced with nitrogen, the color of solution

has faded away into pale brown indicating that most of the carbonyl was incorporated in the resin. The color of resin particles also changed from red to green at the same time. This polymer-supported catalyst was thoroughly washed with aq. dioxane-hexane mixture ($H_2O/dioxane/hexane = 1/30/70$) under nitrogen atmosphere.

The following is a representative procedure for the hydrogenation reaction. Substrate (4 mmol), resin-supported catalyst (5 ml) and aq. dioxane-hexane mixture (15 ml) ($H_2O/dioxane/hexane = 1/30/70$) were weighed into a glass tube which was placed in a 100 ml autoclave. It was then pressurized with 100 kg/cm² of carbon monoxide and heated at 70°C. Conversions and yields were determined either by gas chromatography or product isolation with thin layer chromatography.

Table 1. Selective Hydrogenation Catalyzed by Resin-supported Rhodium Carbonyl^{a)}

No.	Substrate	Product	Reaction Time (hr)	Conversion ^{b)} (%)	Product ^{c)} Yield (%)
1	$C_6H_5-CH=CH-COCH_3$	$C_6H_5-CH_2-CH_2-COCH_3$	9	68	95
2	$C_6H_5-CH=CH-COC_6H_5$	$C_6H_5-CH_2-CH_2-COC_6H_5$	15	84	99
3	$CH_2=CH-COOCH_3$	$CH_3-CH_2-COOCH_3$	5	69	94
4	$CH_2=CH-CN$	CH_3-CH_2-CN	8	39	54 ^{d)}
5	$CH_2=CH-CONH_2$	$CH_3-CH_2-CONH_2$	7	100	100
6	$CH_3-CH=CH-CHO$	$CH_3-CH_2-CH_2-CH_2-OH$	20	100	79
7	1,3-cyclooctadiene	—————	20	~0	—
8	2-octene	—————	20	~0	—

a) Reaction conditions: $Rh_4(CO)_{12}$, 0.031 mmol; Amberlyst A-21, 5 ml; substrate, 4 mmol; aq. dioxane-hexane, 15 ml; CO, 100 kg/cm²; 70°C. b) Based on substrate.

c) Based on conversion. d) The complex partially reacted with acrylonitrile.

When dioxane-hexane mixture was used as solvent, the reaction solution was colorless and no further reaction proceeded in the solution separated from resin particles under the same conditions. Further evidence for the heterogeneity of the catalysis was presented by the fact that the reaction rate was inversely proportional to the volume of solution in which a definite amount of catalyst and a constant concentration of substrate were contained. The resin-supported catalysts can be reused without any appreciable loss in catalytic activity and selectivity.

Various polymeric amine ligands were investigated as support. Amberlyst A-21

and Amberlite IRA-93 which have N,N-dimethylbenzylamine groups were found to be the most excellent polymeric amines in terms of high activity and easy handling. Some results of the hydrogenation with Amberlyst A-21-supported catalyst are summarized in Table 1. This method as well as homogeneous one appears to be of general utility for a wide variety of α,β -unsaturated carbonyl and nitrile compounds. Non-activated double bonds are not hydrogenated as shown in Table 1. In the above reaction conditions, the adjacent carbonyl groups such as ketone, ester and amide, and cyano group are practically intact. However, aldehyde group is hydrogenated to alcohol.⁴⁾ Simple aldehydes such as benzaldehyde and n-butyraldehyde are also hydrogenated to alcohol under the same conditions.

The homogeneous and resin-supported catalyst were compared using various substrates (Table 2). Interestingly the rates with resin-supported catalyst are generally greater than those with homogeneous catalyst.

Table 2. Hydrogenation with Homogeneous Catalyst and Resin-supported Catalyst

Substrate	Reaction Time	Conversion	
		Homogeneous Catalyst ^{a)}	Resin-supported Catalyst ^{b)}
CH ₂ =CH-COOCH ₃	5 (hr)	8 (%)	61 (%)
CH ₂ =CH-CONH ₂	3	11	53
CH ₂ =CH-CN	10	5	34
CH ₂ =CH-COCH ₃	5	33	64
C ₆ H ₅ -CH=CH-COCH ₃	7	12	35
C ₆ H ₅ -CH=CH-COOCH ₃	45	33	20

a) Reaction conditions: Rh₄(CO)₁₂, 0.031 mmol; (C₂H₅)₃N, 5 mmol; substrate, 4 mmol; aq. dioxane-toluene (H₂O/dioxane/toluene = 1/30/70), 15 ml; CO, 100 kg/cm²; 70°C.

b) Reaction conditions: Rh₄(CO)₁₂, 0.031 mmol; Amberlite IRA-93, 1 g (5 mg equiv.); substrate, 4 mmol; aq. dioxane-toluene (H₂O/dioxane/toluene = 1/30/70), 15 ml; CO, 100 kg/cm²; 70°C.

Release of carbon monoxide pressure from the resin-supported catalyst resulted in an instantaneous color change of catalyst beads from red to green. As the IR spectrum in the region of CO stretching frequencies of these green beads is very similar to that of [Rh₆(CO)₁₅]²⁻,⁵⁾ it seems probable that the green beads involve Rh₆ species. On the other hand, only Rh₁₂ species were detected instead of Rh₆ species in homogeneous catalytic system. These observations suggest that

dimerization of the Rh_6 species has been prevented by polymer attachment. We attribute the faster hydrogenation rate of the resin-supported catalyst to the presence of a higher concentration of Rh_6 species which may be true catalyst. Further investigation is now in progress.

REFERENCES and NOTES

- 1) J. C. Bailar, Jr., *Cat. Rev.-Sci. Eng.*, 10, 17 (1974) and references therein.
- 2) Y. Nakamura and H. Hirai, *Chem. Lett.*, 645 (1974); 809 (1974).
- 3) T. Kitamura, N. Sakamoto, and T. Joh, *Chem. Lett.*, 379 (1973).
- 4) In homogeneous catalytic system, aldehydes were partially hydrogenated to alcohol when amines were added.
- 5) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, 102, 344 (1972).

(Received December 16, 1974)