# Colloidal rhodium catalyzed photo transfer hydrogenation of 1,5-cyclooctadiene

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## Abstract

Colloidal rhodium particles, photochemically generated from $Rh_4(CO)_{12}$, via transfer hydrogenation, photochemically catalyzed the transformation of 1,5-cyclooctadiene (1,5-COD) to cyclooctene (COE) and then to cyclooctane (COA) in the presence of acetone, a triplet sensitizer, and 2-propanol, a hydrogen donor. The hydrogenation rate of 1,5-COD was faster than that of COE by a factor of 4.3. Maximum selectivity of COE was found to be 85%.

*Keywords:* Colloidal catalyst; Cyclooctadiene; Dispersion effect; Hydrogenation; Photocatalyst; Rhodium; Selective hydrogenation; Transfer hydrogenation

Colloidal metal particles have recently attracted much attention as a model catalyst for both heterogeneous and homogeneous catalysts. These particles show strong and specific interactions with organic molecules arising from the large specific surface area of the particles [1]. Colloidal noble metals are known to be good catalysts in the hydrogenation of unsaturated organic compounds [2]. In addition, they are effective in photocatalytic reactions, for example hydrogen generation from aqueous solution [3], hydrogenation and photoreduction of dinitrogen to ammonia [4]. In spite of the potential of colloidal material as a component of photocatalyst systems, only a limited number of photocatalytic reactions are reported concerning transformation of organic compounds. Furthermore, the nature of colloidal metal species in photocatalytic reactions has not been investigated in detail.

One problem with colloidal metal when used as a catalyst [2] is that the colloidal material usually requires a polymer reagent to be stable, such as polyvinylpyrrolidone or polyethylene glycol. In the absence of a polymer, colloidal particles easily aggregate and lose catalytic activity. However, polymer stabilizers often cover active sites on the surface which reduces catalytic activity [5].

We have been investigating the preparation of colloidal noble metals, that do not require the addition of polymer stabilizers, and the possibility of their use as nobel metal photo-related catalysts. Previously, systems consisting of colloidal noble metals and triplet sensitizers were found effective for photocatalysis in dehydrogenative dimerization of alcohol and cyclic ethers [6]. We report a

i) Acetone, 2-PrOH, Colloidal Rhodium

Scheme 1.



Fig. 1. Time course of the photocatalytic transfer hydrogenation of 1,5-cyclooctadiene. Precursor of colloidal catalyst, $Rh_4(CO)_{12}$, 2.0 mg was used. 1,5-Cyclooctadiene (1,5-COD) was added after 60 min irradiation. (O) 1,5-COD, (△) 1,4-COD, (●) COE, (□) COA.
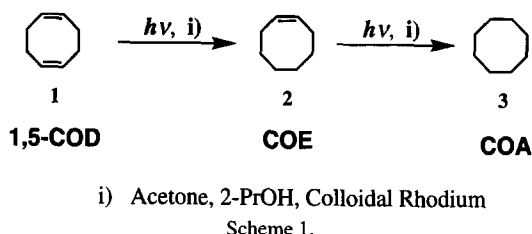
photo-derived transformation of $Rh_4(CO)_{12}$ to highly dispersed colloidal rhodium particles and their application to a photocatalytic transfer hydrogenation of 1,5-cyclooctadiene (1,5-COD) to cyclooctene (COE) and cyclooctane (COA) in the presence of acetone and 2-propanol [7] (Scheme 1).

On photocatalytic transfer hydrogenations of 1,5-COD, a deaerated solution of acetone (8.0 cm³), 2-propanol (32.0 cm³) and an adequate amount of $Rh_4(CO)_{12}$ were placed in a cylindrical quartz cell (50 mm diameter and 40 cm³ cell volume). The cell was irradiated by a 500 W high pressure Hg lamp (Ushio Inc.) through a UV-25 (Toshiba, 40% transmittance at 250 nm) optical cut-off filter. After five minutes irradiation, the color of the solution changed from pale rose-red to dark brown, as a result of the formation of colloidal species, and $H_2$ gas evolution was observed.

Formation of colloidal rhodium was confirmed by electronic spectra of reaction solution. Characteristic absorption of $Rh_4(CO)_{12}$ at 350 nm disappeared rapidly through irradiation, then a broad and structureless absorption band appeared. This absorption can be assigned to a scattering band of colloidal metals. It was estimated that photodecomposition of $Rh_4(CO)_{12}$ occurred at first and was followed by growth of colloidal particles. The colloidal dispersion was stable for several days after photoreaction even in absence of a polymer stabilizer.

In order to complete transformation of carbonyl complex to colloidal species, 1,5-COD (0.3 cm³) was added to reaction solution after one hour's irradiation. Photo-transfer hydrogenation of 1,5-COD proceeded smoothly to COE and then to COA. Although addition of 1,5-COD reduced the
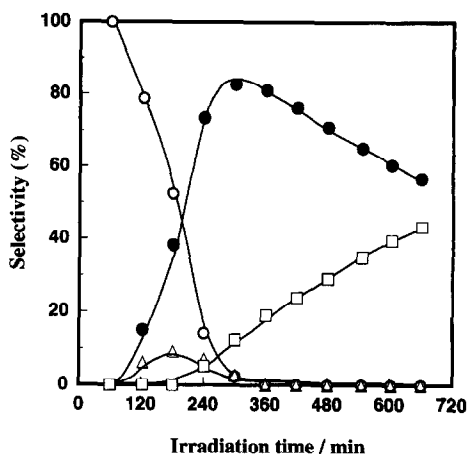
$H_2$ evolution rate to ca. 70% of the rate of the initial stage, the evolution did not stop during the photocatalytic transfer hydrogenation [1]. The gas evolved was collected with a gas buret and analyzed by gas chromatography equipped with TCD. Photocatalytic products were also analyzed by gas chromatography using a TC-WAX capillary column (GL Science Inc., Tokyo).

The typical result of the photocatalytic transfer hydrogenation of 1,5-COD are shown in Fig. 1 as the change of products composition by irradiation. Maximum selectivity [2] of COE was over 85%. Isomerized product 1,4-cyclooctadiene (1,4-COD) was observed only in the early stage and its maximum selectivity was ca. 8.5%. By contrast, another isomerized product, 1,3-cyclooctadiene (1,3-COD), was not detected during the reaction. This may be attributed to the rapid hydrogenation of conjugated diene such as 1,3-COD compared with non-conjugated diene such as 1,5-COD and 1,4-COD. Pinacol and radical coupling

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[1] By control experiments, every component, $Rh_4(CO)_{12}$, irradiation with UV light and alcohol was confirmed to be necessary for both hydrogenation and $H_2$ evolution.

[2] Selectivity of COE

$$= \left( \frac{\text{Yield of COE}}{\text{Yield of (1,5-COD + COE + COA + 1,4-COD + 1,3-COD)}} \right)$$

$\times 100$

Table 1
Effect of catalyst precursor's concentration on photocatalytic activities

| $Rh_4(CO)_{12}$/mg | $H_2$ evolution rate [a]/mmol·h$^{-1}$ | Selectivity of COE [b] (%) | Rate of 1,5-COD to COE [c]/ mmol·h$^{-1}$ | TOF of 1,5-COD to COE/ h$^{-1}$ |
|---|---|---|---|---|
| 0.5 | 3.4 | 80.0 | 0.71 | 259.8 |
| 1.0 | 3.4 | 81.2 | 0.78 | 145.7 |
| 2.0 | 3.1 | 85.2 | 0.43 | 40.4 |
| 3.0 | 2.3 | 85.6 | 0.26 | 16.0 |
| 6.0 | 0.7 | 69.0 | 0.1 | 3.1 |

Reaction conditions: light source, 500 W high pressure Hg lamp (UV-25 filter, Toshiba); acetone, 8.0 cm$^3$; 2-propanol, 32.0 cm$^3$; 1,5-COD, 0.3 cm$^3$.
[a] $H_2$ evolution rate before addition of 1,5-COD.
[b] Maximum selectivity.
[c] Based on a pseudo 1st order estimation of hydrogenation rate before consumption of 1,5-COD.

products between hydroxy radical and cyclooctane moiety were observed in low yields as by-products. As a result of the formation of by-products, the yield of COA was reduced to ca. 65–75%

The transfer hydrogenation rate of 1,5-COD was much faster than that of COE. The ratio of the reaction rates between '1,5-COD to COE (just after addition of 1,5-COD)' and 'COE to COA (after consumption of 1,5-COD)' was estimated from the reaction data based on a pseudo first order reaction. The ratio of the rates was ca. 4.8 in the photocatalytic transfer hydrogenation with rhodium colloid catalyst as shown in Fig. 1. By individual experiments, photocatalytic transfer hydrogenation of COE alone, the hydrogenation rate of COE was similar to the rate in the successive hydrogenation, which is shown in Fig. 1. The differences in the rates of both steps are attributable to the degree of affinity between olefins and the surface of the colloidal rhodium.

Table 1 exhibits influences of the concentration of $Rh_4(CO)_{12}$ on transfer hydrogenation and $H_2$ evolution. Both rates decreased with increasing catalyst concentration. For example, when using 0.5 mg of $Rh_4(CO)_{12}$ ([Rh] = 1.7 × 10$^{-6}$ mol·l$^{-1}$), the $H_2$ evolution rate was 3.4 mmol·h$^{-1}$ before addition of 1,5-COD, and hydrogenation rate of 1,5-COD was 0.70 mmol·h$^{-1}$. But when 2.0 mg was used ([Rh] = 6.7 × 10$^{-5}$ mol·l$^{-1}$), these reaction rates were decreased to 3.1 and 0.43 mmol·h$^{-1}$,

respectively. These rates were further decreased to 0.70 and 0.1 mmol·h$^{-1}$, respectively when 6.0 mg was used ([Rh] = 2.0 × 10$^{-4}$ mol·l$^{-1}$).

The TOF value [3] of 1,5-COD to COE was also decreased with increasing concentration, 259.8 h$^{-1}$, 40.4 h$^{-1}$ and 3.1 h$^{-1}$, respectively. The hydrogenation rate was found to be much lower than the rate of hydrogen evolution, especially when a high concentration of catalyst was used. Hydrogen transfer to COD and/or adsorption of olefins on the colloidal surface were effective at lower concentrations of colloidal catalyst.

It is known that the catalytic properties of rhodium particles are affected by the degree of dispersion [8]. Thus, the increase of catalyst activity at lower concentrations is probably due to the higher degree of dispersion of the colloidal catalyst. As the degree of aggregation is strongly related to the concentration of precursor, we see that at lower concentrations, growth of particles is slower than that at high concentrations. Moreover, at lower concentrations, aggregation of particles is inhibited by diffusion. Because a large proportion of surface atoms is found in highly dispersed colloidal particles compared to aggregated ones, it is probable that these colloidal catalysts show higher specific activity at lower concentrations. Additionally, the life of intermediate radicals seems to be affected by diffusion factors in this reaction.

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[3] Turnover frequency: number of molecules (of 1,5-COD) hydrogenated per rhodium atom used per unit time.
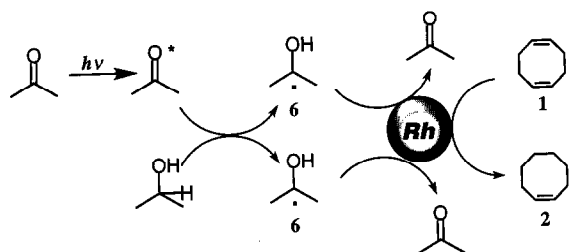
Scheme 2.

Selectivities of the hydrogenation were also changed with the concentration of catalyst precursor. Maximum selectivities of COE varied from 85% to 69% depending on the concentration of catalyst. The effect on selectivity was smaller than that on the activity of transfer hydrogenation. It seemed that the small effect on selectivity by change in particle size was due to the structure insensitivity of the rhodium catalyst in the hydrogenation of olefin [8].

To explain these results, we propose the mechanism of the photocatalytic cycle as depicted in Scheme 2. Reaction is initiated by $\alpha$-hydrogen abstraction from alcohol (2-propanol) with triplet excited acetone, and two 1-hydroxy-1-methylethyl radicals are formed. These radicals transfer hydrogen atom to colloidal species through an electron transfer process [3]. Based on the effect of catalyst concentration and the difference of hydrogenation activity between 1,5-COD and COE, formation of $H_2$ molecule and hydrogenation of olefins occur on surface of colloidal rhodium. Affinity between the surface of colloidal metal and the substrate is an important factor for reaction performances on these catalysts [9].

Thus, it is concluded that the modification of surface and substrate could elucidate the interaction on the surface in order to control the reaction on colloid catalysts [10].

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