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Preparation of Size-controlled Ruthenium Metal Particles on Carbon from Hydrido-carbonyl Cluster Complex

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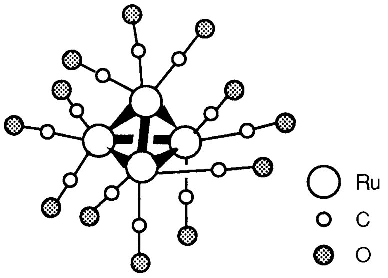
Monodispersed ultrafine particles of metallic ruthenium (1.3 and 2.1 nm in average diameters) were prepared by heating and stirring the mixed powders of hydrido-carbonyl cluster $H_4Ru_4(CO)_{12}$ and microporous carbon at 433 K under H_2 flow. It was revealed that high dehydrogenation activities for 2-propanol were obtained over large ruthenium metal particles rather than small ones prepared with this dry method.

Preparation of monodispersed ultrafine particles has attracted considerable attention especially on metals.1) Reduction of metal salts in the presence of surfactants with or without photoirradiation was successfully attempted for gold2) or platinum3) colloids. As for the preparation of metal catalysts, the important role of metal carbonyl precursors has been pointed out,4) as halogen impurities are completely excluded.

In the present work, monodispersed ultrafine ruthenium metal particles are successfully prepared from a hydrido-carbonyl cluster complex and microporous activated carbon, which has significance in getting highly-active dehydrogenation catalysts for 2-propanol5) indispensable to a newly-proposed chemical heat pump system.6)

Metal particles were supported on KOH-activated carbon (BET specific surface area : 3100 m^2 g^{-1}, dominant pore diameter : 2.0 nm, pore volume : 1.78 cm^3 g^{-1}, Kansai Netsukagaku Co.).7) Catalytic activities of ruthenium for 2-propanol dehydrogenation were examined in a suspended state under boiling and refluxing conditions. The amounts of product hydrogen were monitored with a gas burette. Diffused reflectance FT-IR spectroscopy could detect the carbonyl clusters on surface. The reaction products were analyzed by gas chromatography with active-carbon (gas phase) and PEG-20M (liquid phase) columns, respectively. The size and spatial distributions of catalyst particles were obtained from TEM images (Hitachi H-700H; magnification 100 000).



Dodecacarbonyltetra-μ–hydrotetraruthenium

A non-sublimable cluster complex $H_4Ru_4(CO)_{12}$ (mp 463 K) was obtained from a sublimable complex

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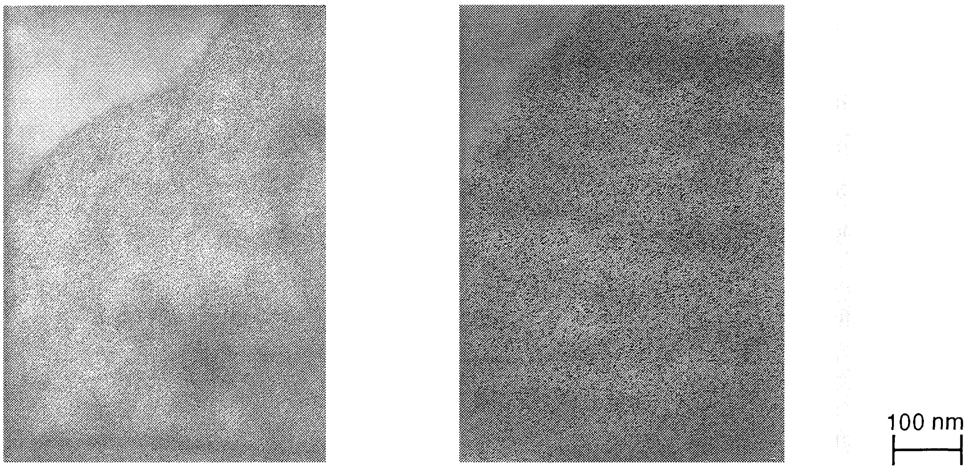
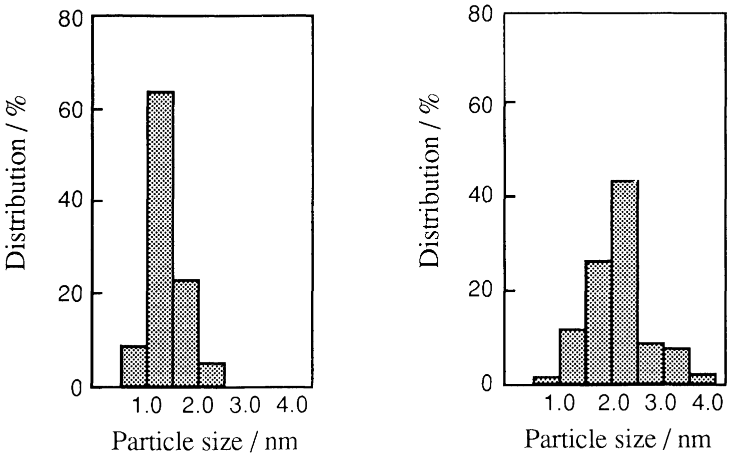
$Ru_3(CO)_{12}$ by passing hydrogen through its octane solution at 363 K for 1 h.[8] A powder mixture of carbon and $H_4Ru_4(CO)_{12}$, purified with chromatographic column separation,[8] was heated at 433 K under the gas flow of argon or hydrogen for 1 h and evacuated.

The CO dissociation from the carbon-loaded complex, which was prerequisite to catalysis for 2-propanol dehydrogenation, began at 388 K and completed at 433 K according to gas chromatography. The carbonyl IR peak disappeared at this temperature range as well. Insufficient dissociation of CO was observed from the same complex at the same temperature range, as far as the impregnation method was adopted for catalyst preparation from the $H_4Ru_4(CO)_{12}$ solutions of methanol, cyclohexane, and 2-propanol.



(A) Ru / carbon: 5 wt% (B) Ru / carbon: 17 wt%

Fig. 1. TEM photomicrograph of $H_4Ru_4(CO)_{12}$. Magnification is 100 000.



(A) Ru / carbon: 5 wt% (B) Ru / carbon: 17 wt%

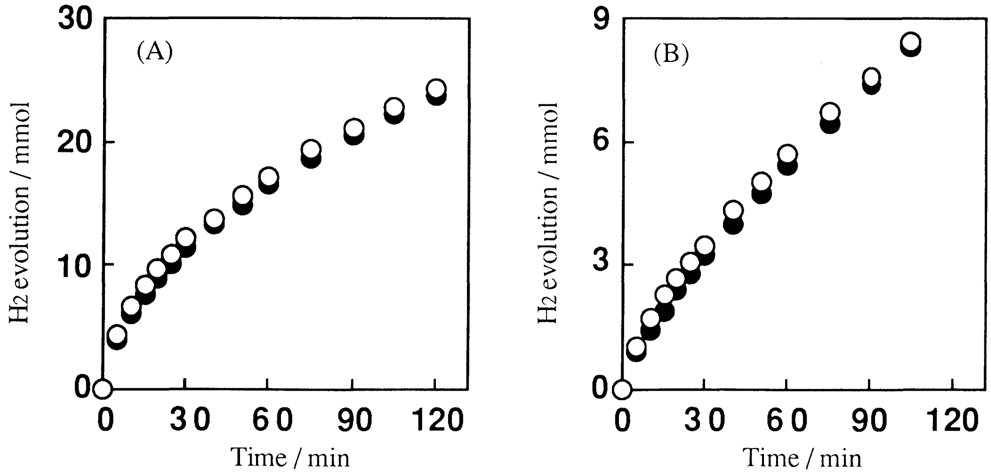
Fig. 2. Carbon-supported ruthenium metal catalyst prepared from $H_4Ru_4(CO)_{12}$ by dry method under H_2 flow.

As evident from TEM images(Fig. 1), spatial distributions of ruthenium metal particles prepared with this dry method were surprisingly uniform. We observed no metal particles grown outside or at the outer surface of the carbon granule.

Sharp or monodispersed particle-size distributions were apparent (Fig. 2), especially when a small amount of $H_4Ru_4(CO)_{12}$ (5 wt% as Ru/C) was loaded. Moreover, it was demonstrated that particle sizes were controllable by changing the concentrations of the cluster complex.

The growth mechanism of metal particles would be closely related to the observed coincidence between particle sizes and cluster concentrations. Provided that one carbon micropore (dominant pore diameter : 2.0 nm) contained one cluster complex (estimated diameter : 1.7 nm) at most and that the cluster complexes were distributed to the micropores uniformly inside the carbon granule, the concentrations of ruthenium metal per pore volume were calculated as 0.030 and 0.118 g cm^{-3} for the samples of ruthenium-loaded-on-carbon at 5 and 17 wt%, respectively. Since the average particle diameters of monodispersed ruthenium metal were 1.3 and 2.1 nm for these samples, the heat treatments at 433 K for 1 h toward the cluster complex inside the micropore under the dry-mixing conditions would cause the complex decomposition and metal-cluster migration, followed by coagulation into metal particles. Interestingly, the formation of one metal particle was attributed to this migration from the micropores immersed with the complex in the ranges of 16.0 and 15.6 nm cubes for the 1.3 and 2.1 nm particles, respectively. On the basis of the diffusion-controlled mechanism for particle growth,9) the transport distance of material would be common under the same heating conditions of medium carbon granules. Size control of monodispersed ultrafine ruthenium metal particles has thus been successfully accomplished for the first time under mild conditions.

The two kinds of Ru/carbon catalysts dehydrogenated 2-propanol under boiling and refluxing conditions, as depicted in Fig. 3(A), where similar activities per metal in weight basis were demonstrated between the catalysts with different particle sizes (1.3 and 2.1 nm, see Table 1). Rate retardation caused by the product acetone was shown in Fig. 3(B). Insensitivity toward acetone is required for high thermal efficiency and compact system design in the chemical heat pump system.



E : Ru/C catalyst (17 wt%, 2.1 nmf) J : Ru/C catalyst (5 wt%, 1.3 nmf)

Solution : (A) 2-Propanol (100 ml), (B) 2-Propanol (98 ml) + acetone (2 ml).
Catalyst: 0.05 mmol as Ru species prepared from $H_4Ru_4(CO)_{12}$
Reaction conditions: Boiling and refluxing(82.4 °C).

Fig. 3. Dehydrogenation of 2-propanol with carbon-supported Ru catalyst.

Table 1. 2-Propanol Dehydrogenation over Monodispersed Ruthenium Metal Catalyst

Carbon-supported Ru Catalyst			Reaction Rate Parameter		
Loaded amount	Average size	Metal surface area	Rate constant		Retardation constant
wt%	nm	$m^2 \cdot g^{-1}$	$mol \cdot h^{-1} \cdot g^{-1}$	$mol \cdot h^{-1} \cdot m^{-2}$	$dm^3 \cdot mol^{-1}$
17	2.1	116	4.77	0.410	12.7
5	1.3	188	4.28	0.228	12.2

Catalyst preparation : $H_4Ru_4(CO)_{12}$ and carbon stirred at 160 ℃ under H_2 atmosphere.
Reaction conditions : Boiling and refluxing (82.4 ℃) under external heating at 100 ℃.

A Langmuir-type rate equation, $v = k / (1 + K[\mathrm{acetone}])$, was applied aptly to catalytic 2-propanol dehydrogenation, where k and K are the rate constant and the retardation constant induced by the product acetone, respectively. By comparing the rate constant per metal surface area, the activity of large metal particles was suggested to be higher (0.410 mol $h^{-1}m^{-2}$) than that of small ones (0.228 mol $h^{-1}m^{-2}$). If metal particles embedded in the carbon micropores were too small to have adequate contact with the substrate in the solution, the rate constant of the ruthenium catalyst would be diminished. A slight difference between the 2.1 and 1.3 nm samples on the rate retardation due to acetone was comfirmed by use of 2-butanone addend (18.6 and 17.6 dm^3mol^{-1}, respectively), being similar with respect to the 2-butanol formation caused by hydrogen transfer from 2-propanol to 2-butanone (5.21 and 6.21 $h^{-1}g^{-1}$, respectively).

In conclusion, a new preparation method of monodispersed ultrafine ruthenium particles under dry-mixing and heating conditions has made it possible to control the metal sizes and catalytic characteristics.

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