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Preparation of Fine-particle Platinum-ruthenium Composite Catalyst Highly-active for Liquid-phase Alkane Dehydrogenation

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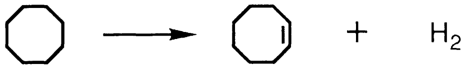
A Pt-Ru metal composite catalyst prepared from complexes with different charges, $[Pt_3(CO)_6]_5^{2-}$ and $[(C_6Me_6)_2Ru]^{2+}$, exhibited monodispersed distribution with respect to particle size and composition. A synergetic effect on ethylcyclohexane dehydrogeno-aromatization was well demonstrated under boiling and refluxing conditions, contrary to the case prepared from $[Pt_3(CO)_6]_5^{2-}$ and neutral $Ru_3(CO)_{12}$.

The reaction of alkane dehydrogenation yielding alkene and molecular hydrogen under mild conditions has been one of the most challenging targets in catalytic chemistry.1) Homogeneous2) and heterogeneous3) catalysts active for cyclooctane(eq. 1) and even cyclohexane(eq. 2) dehydrogenation were found. However, the catalytic activities remain still at unsatisfactory levels.


(1)


(2)

A synergetic effect on dehydrogeno-aromatization of cyclohexanes under boiling and refluxing conditions was accomplished by use of a platinum-ruthenium composite catalyst prepared from the mixed chlorides.4) Gallezot et al. had prepared carbon-supported platinum-ruthenium bimetallic catalysts with various compositions from $[Pt(NH_3)_4]^{2+}$ and $[Ru(NH_3)_2]^{3+}$ by an ion-exchange method, investigating the activity and selectivity for cinnamaldehyde hydrogenation.5)

In the present work, a pair of differently-charged ionic complexes, $[Pt_3(CO)_6]_5^{2-}$ 6) and $[(C_6Me_6)_2Ru]^{2+}$,7) is adopted as catalyst precursors, aiming at a synergy design of dehydrogeno-aromatization catalysts for cyclohexanes.

Unsaturated impurities in ethylcyclohexane were removed by stirring with conc. HNO_3 and H_2SO_4, water-washing, $CaCl_2$-drying and finally being distilled in the presence of Na under N_2 atmosphere. A KOH-activated carbon8)(BET specific surface area: 3100 m^2g^{-1}, Kansai Netsukagaku Co.) was heated under H_2 for 2 h and evacuated for 20 min just before preparing the four kinds of metal catalysts(Scheme I), including the Pt:Ru = 15:1(atomic ratio) composite. H_2 evolution from the catalyst suspension of ethylcyclohexane under boiling and

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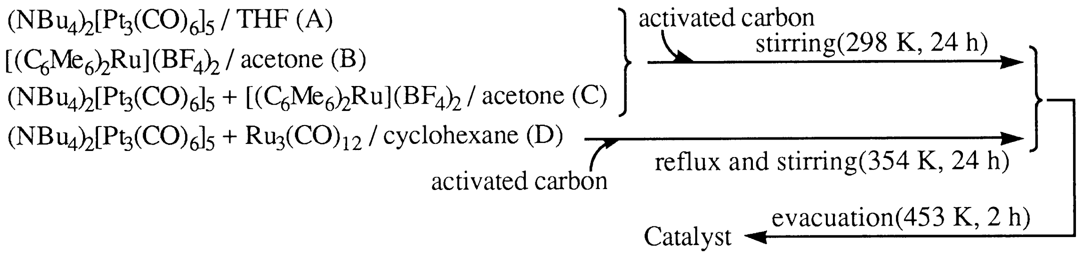

Scheme 1. Preparation of platinum or platinum-ruthenium catalyst supported on carbon.

refluxing conditions(405 K) was pursued volumetrically with a gas burette. Gaseous and liquid-phase components were analyzed by gas chromatography, using active carbon and PEG-20M capillary columns, respectively. Spatial and size distributions were obtained from TEM images(Hitachi H-700, maginf. 100000). Transmission electron microscopy of field-emission type and energy dispersive X-ray emission(EDX) with the Pt-Mα and Ru-Lα lines were utilized for determining the composition of the metal particles(Hitachi HF-2000, magnif. 300000).

TEM images of Catalyst C and D are contrasted in Fig. 1. The metal particles of Catalyst C were dispersed uniformly inside the carbon granule without aggregation. As shown in Fig. 2, sharp particle-size distribution of Catalyst C(1.4 nm in average) was apparently different from Catalyst D, which contained both small and fairly large particles (1.9 nm in average).

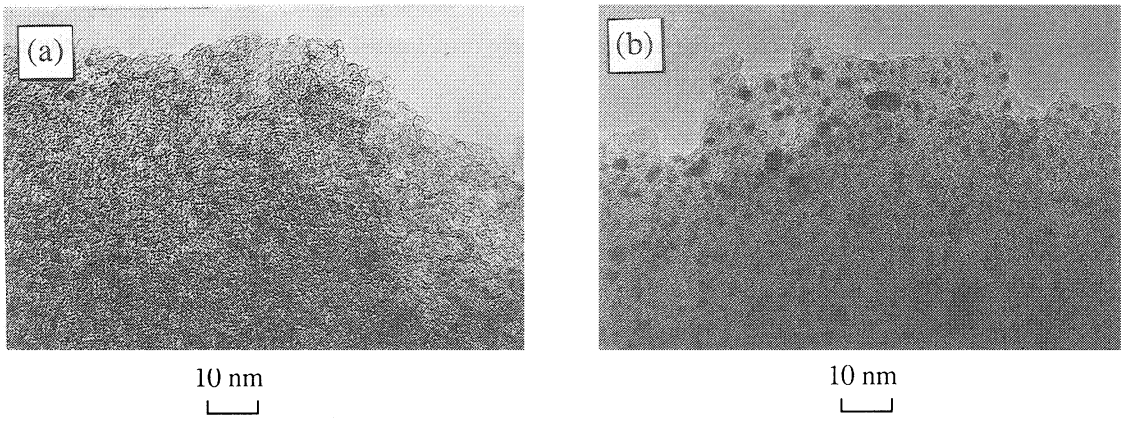

Fig. 1. TEM images of Catalyst C(a) and D(b).

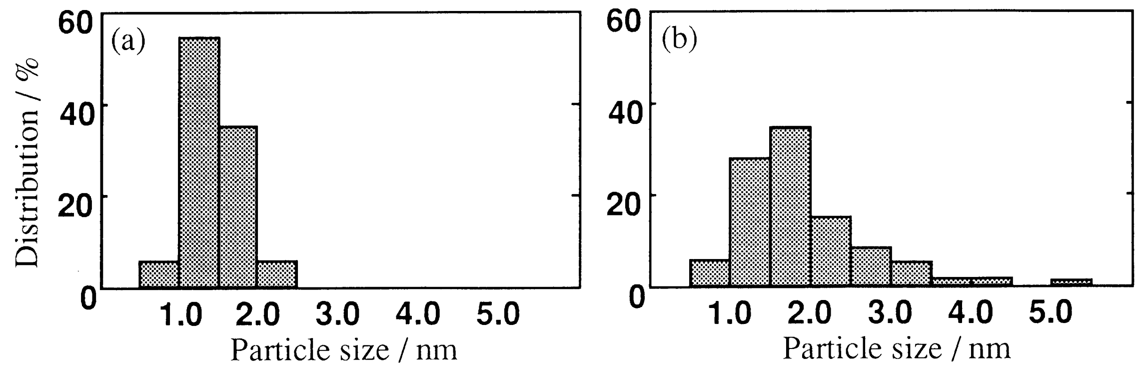

Fig. 2. Particle size distribution of carbon-supported platinum-ruthenium catalyst prepared from $(NBu_4)_2[Pt_3(CO)_6]_5 + [(C_6Me_6)_2Ru](BF_4)_2$ (Cat. C, (a)) and $(NBu_4)_2[Pt_3(CO)_6]_5 + Ru_3(CO)_{12}$ (Cat. D, (b)).

Metal particle sizes and atomic Ru fractions obtained from the characteristic X-rays spectra(EDX) were correlated as Fig. 3 for the two kinds of Pt-Ru composite catalysts. The magnitudes of Ru fraction were determined by appropriate atomic-weight corrections on the Pt and Ru peak areas and the calculated Ru fraction as the ionic pair(6.25 %).

The sharp distributions of size and composition observed for the metal particles of Catalyst C were contrasted to Catalyst D as a mixture of two kinds of metal particles; small particles with high Ru contents and rather large particles with low Ru fraction.

The Pt, Ru and Pt-Ru composite catalysts dehydrogenated ethylcyclohexane, as shown in Fig. 4. Dehydrogenated products in the solution were found to be exclusively ethylbenzene, accompanied with no byproducts such as styrene, cyclohexenes and cyclohexadienes. The evolved gas was solely composed of H_2. Since the metal particles were grown, no CO had been detected in the gas phase. The amounts of H_2 and ethylbenzene were stoichiometrically reasonable(Table 1).

Catalyst C(Pt-Ru metal composite, turnover number(T.O.N., 12 h) 40.8 per metal atom(total)) gave the highest activity among these catalysts. Comparable activities of Catalyst D and Catalyst A(Pt metal, T.O.N.(12 h) 4.58) were higher than that of Catalyst B(Ru metal, T.O.N.(12 h) 0.27). The cationic and anionic pair complexes, $[(C_6Me_6)_2Ru]^{2+}$ and $[Pt_3(CO)_6]_5{}^{2-}$, extended excellent synergetic catalysis. The mixture of anionic($[Pt_3(CO)_6]_5{}^{2-}$) and neutral ($Ru_3(CO)_{12}$) complexes were ineffective as the pair of catalyst precursors(Catalyst D).

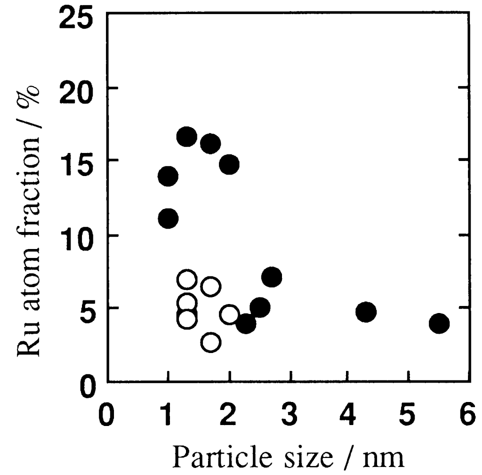

Fig. 3. Particle size(TEM) and composition analysis (EDX) on two kinds of Pt-Ru/C catalysts prepared from $(NBu_4)_2[Pt_3(CO)_6]_5$ + $[(C_6Me_6)_2Ru](BF_4)_2$ (cat. C, E) and $(NBu_4)_2[Pt_3(CO)_6]_5$ + $Ru_3(CO)_{12}$ (cat. D, J).

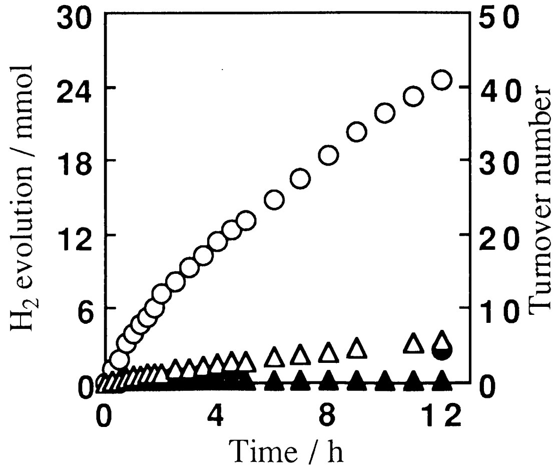

Fig. 4. H_2 evolution from ethylcyclohexane using the catalyst prepared from $[Pt_3(CO)_6]_5{}^{2-}$(A, J), $[(C_6Me_6)_2Ru]^{2+}$(B, H), $[Pt_3(CO)_6]_5{}^{2-}$ + $[(C_6Me_6)_2Ru]^{2+}$ (C, E), and $[Pt_3(CO)_6]_5{}^{2-}$ + $Ru_3(CO)_{12}$ (D, C) in a suspended state (0.2 mmol-metal/100 cm^3) under boiling and refluxing conditions (405 K).

A Pt-Ru composite catalyst prepared by an impregnation method from K_2PtCl_4 and $RuCl_3$ consisted of metal particles with various Pt/Ru ratios and sizes(2.6 nm in average).[9] It is important to have any preparation method of metal composite catalysts, for which uniform composition as well as monodispersion concerning spatial and size distributions are assured.

As the precursor complexes of Catalyst C are both anionic and cationic, an ion pair of $[Pt_3(CO)_6]_5{}^{2-}$-$[(C_6Me_6)_2Ru]^{2+}$ will be formed either in solution or inside the hydrophilic micropores of supporting carbon, which is in contrast to Catalyst D, prepared from hydrophilic $[Pt_3(CO)_6]_5{}^{2-}$ and hydrophobic $Ru_3(CO)_{12}$. Activated carbon is made from disordered aromatic crystallites connected three-dimensionally by aliphatic hydrocarbons, oxygenic functional groups being attached on the prismatic planes.[10)] As the inner surfaces of carbon micropores are both hydrophobic and hydrophilic, polar ionic pairs will adsorb selectively on the hydrophilic region in contrast to the pair of ionic and neutral cluster complexes. The thermal redox decomposition of precursor complexes will be followed by coagulation and crystal growth on the carbon granule. Monodispersed ultrafine metal particles of Catalyst C, keeping the composite ratio of Pt:Ru=15:1, would thus be formed. In Catalyst D, however, the growth of multidispersed metal particles with respect to spatial, size and constitutional distributions were inevitable, since attractive interactions were unexpected for the pair of $[Pt_3(CO)_6]_5^{2-}$ and $Ru_3(CO)_{12}$. The growth of small ruthenium-rich metal particles(Fig. 3) would be inherited from the property of $Ru_3(CO)_{12}$ itself.

Table 1. Dehydrogenation of ethylcyclohexane with Pt or Pt-Ru catalyst supported on carbon[a)]

Catalyst	Time / h	Product / mmol	
		H_2	Ethylbenzene
A	12	2.75	0.92
B	12	0.16	0.00
C	12	24.5	6.82
D	12	3.44	0.82

a) Catalyst solution: 0.2 mmol-metal / 100 cm^3.
Reaction conditions: Boiling and refluxing (405 K).

The composite ratios of Ru:Pt can be varied along the present approach of catalyst preparation by adopting $[(C_6Me_6)_2Ru]^{2+}$ and the series of $[Pt_3(CO)_6]_n^{2-}$(n = 1-10).[6)]

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