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A Composite Ru-Pt Catalyst for 2-Propanol Dehydrogenation Adoptable to the Chemical Heat Pump System

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Synergetic promotion was observed for 2-propanol dehydrogenation with a composite Ru-Pt/carbon catalyst, prepared by $NaBH_4$ reduction of mixed metal chlorides adsorbed on active carbon in an aqueous solution. Metal crystallites were less than 2 nm in size. The pronounced rate is promising as the catalyst for the heat pump system.

In the newly-proposed chemical heat pump system, aiming at the conversion of low-quality waste heat (80 ℃) into more valuable one (200 ℃) at the sacrifice of partial cooling (30 ℃),[1] preeminent catalysts are most essential, especially for endothermic dehydrogenation of 2-propanol performed at low temperatures under refluxing conditions.

$$(CH_3)_2CHOH(l) \longrightarrow (CH_3)_2CO(g) + H_2(g) \quad (1)$$

The dehydrogenation catalyst in a well-dispersed state should be active in the presence of a certain amount of acetone, because compact volumes are anticipated for the liquid-phase reactor as well as for the distillation column, where the separation of gaseous acetone and hydrogen from condensed 2-propanol is performed.

Recently it was revealed that metallic ruthenium supported on carbon (designated hereafter as Ru/carbon) gave a tremendously high catalytic rate for 2-propanol dehydrogenation, whereas the Pt/carbon catalyst was insensitive to the rate retardation caused by acetone adsorption.[2]

In view of these characteristic advantages of the Ru/carbon and Pt/carbon catalysts, we attempted here to prepare a composite Ru-Pt/carbon catalyst by reducing the aqueous solution of mixed metal chlorides after adsorption onto active carbon powders.

Active carbon powders (2 g, BET specific surface area: 2770 m^2/g, Kansai Netsukagaku Co.) were impregnated with the aqueous solutions of $RuCl_3 \cdot 3H_2O$ (Wako Pure Chem. Co.) and K_2PtCl_4 (Kojima Kagaku Co.) mixed in the atomic ratios of Ru/Pt = 1/0, 4/1, 1/1, 1/4, and 0/1 for 6-8 h at room

temperature. The adsorbed metal salts (5 wt% as metal) were reduced in a suspended state with the aqueous solution of $NaBH_4$ (900 mg/10 ml) by adding it dropwise (1 ml / min). After standing for about 10 min, the carbon-supported catalyst was filtered and washed with a large amount of water in order to remove the residual sodium and chloride ions as well as boric acid. The catalyst was evacuated for 10 h at 50 ℃ before use.

The reaction of 2-propanol dehydrogenation was analyzed with the apparatus and procedure reported previously.[3] The catalyst (100 mg) thus prepared was dispersed in 2-propanol (100 ml) ultrasonically (Kaijo Denki Co., Sona 50a) for 5-7 min in a three-necked round-bottom flask (300 ml). After substituting the atmosphere with flowing N_2 gas, the reactor was heated by an oil bath (100 ℃) to boil the suspended solution vigorously at 82.4 ℃ under refluxing conditions (20 ℃). The amount of hydrogen was measured for the reaction time of 2 h by a gas burette. The initial reaction rate was determined from the volume increment during the period of 10-15 min after the start of the reaction, where the thermal inflation of volume was corrected. The reaction products were identified during and after the reaction with gas chromatography using MS-13X and Porapak Q columns for gases and a PEG 20M column for liquid-phase components.

It was proved that higher catalytic activities for 2-propanol dehydrogenation were attained per metal weight with the composite Ru-Pt/carbon catalysts in comparison to non-composite ones (Fig. 1). The gaseous and liquid-phase products of Ru/carbon were exclusively hydrogen and acetone, which were formed with excellent stoichiometry.

The reaction rates of 2-propanol dehydrogenation by suspended catalysts have been well described with the following rate equation.[4,5]

$$v = k / (1 + K[\text{acetone}]) \quad (2)$$

In the present analysis, the rate constant k was taken to be equal to the observed initial rate, while the retardation constant K was determined from the relationship (Eq. 2) by substituting the amount of acetone with that of hydrogen at

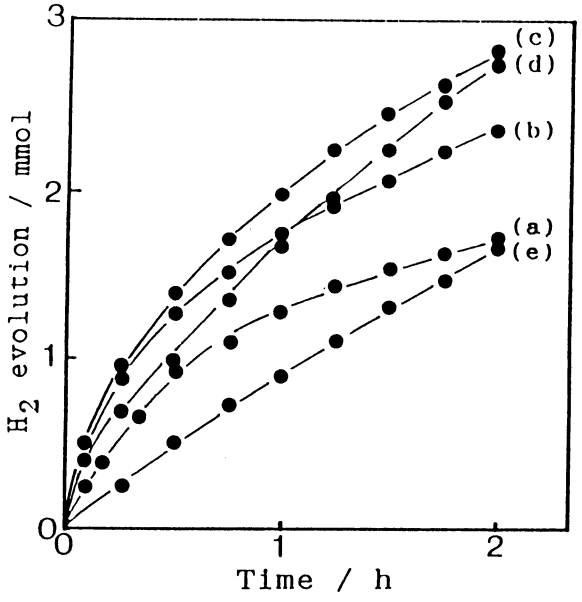

Fig. 1. Time course plots of 2-propanol dehydrogenation with suspended ruthenium, platinum and composite catalysts.
(a) Ru, (b) Ru/Pt = 4/1, (c) Ru/Pt = 1/1, (d) Ru/Pt = 1/4, and (e) Pt.

Table 1. Rate constant of 2-propanol dehydrogenation and retardation constant due to product acetone for suspended ruthenium, platinum and composite catalysts

Ru/Pt atomic ratio	Rate constant k / mol h^{-1} g^{-1}	Retardation constant K / mol^{-1} m^3
1/0	2.17	13.2
4/1	3.16	13.0
1/1	4.01	10.6
1/4	3.29	3.44
0/1	1.78	2.28

each reaction time. As shown in Table 1, the rate constant k exhibited a synergetic effect with a maximum in the middle region, whereas the retardation constant K was diminished gradually with the increase of Pt content.

It was also demonstrated that the synergetic effect on the initial rate, observed for the composite Ru-Pt/carbon catalyst, was not achieved by the mechanical mixture of Ru/carbon and Pt/carbon catalysts (Fig. 2).

Nickel fine particles, prepared by the gas-evaporation technique, were reported previously to take a promising role in the chemical heat pump system as the liquid-phase catalyst for 2-propanol dehydrogenation.[5] Conspicuous improvement has now been brought about with the composite Ru-Pt /carbon catalyst. Not only the rate constant k but also the retardation constant K of the composite Ru-Pt(1/1)/carbon catalyst (4.01 mol g^{-1} h^{-1}, 10.6 mol^{-1} m^3) were far better than the corresponding values of the Ni fine-particle catalyst (0.094 mol g^{-1} h^{-1} and 46.0 mol^{-1} m^3), all of which were obtained from the experiments with a common basis of 2-propanol amount (100 ml).[6]

The catalysts were characterized with the powder X-ray diffraction method using a Rigaku Denki Geigerflex diffractometer (Radiator: D-9C, Goniometer: SC-7) with CuKα radiation (Table 2). The Ru/

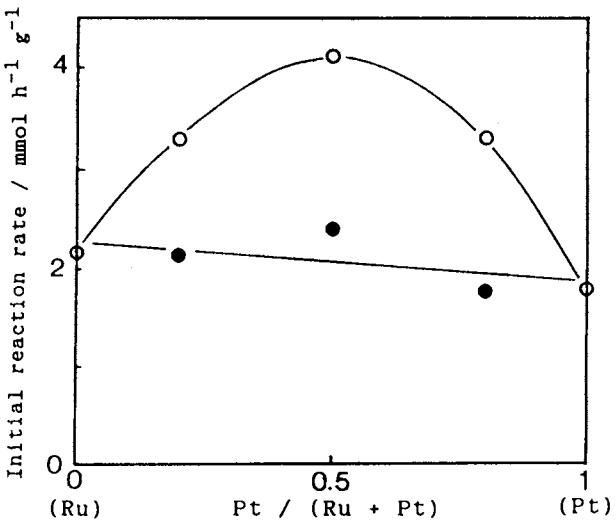

Fig. 2. Initial reaction rates of 2-propanol dehydrogenation with pcomposite and mechanically mixed Ru-Pt/carbon catalysts.
(O) Ru-Pt composite catalyst,
(●) Ru and Pt mixed catalyst.

Table 2. Crystallite size of carbon-supported metal catalyst

Catalyst	Miller index	Diffraction angle 2 θ(cor.)	Crystallite size L / nm	Lattice spacing d / nm obs. (bulk)
Pt	(111)	39.63	1.4	0.227 (0.227)
	(200)	45.83	1.9	0.198 (0.196)
Ru	(101)	43.37	1.5	0.139 (0.139)
Ru-Pt	Pt(220)	67.56	2.0	0.118 (0.118)
	Pt(311)	81.52	1.9	0.209 (0.206)

carbon, Pt/carbon and Ru-Pt(1/1)/carbon samples were ground and pressed onto an Al holder. The 2θ calibration was made with Si particles (99.9999 %, uniform size distribution). Broad peaks corresponding to Pt (111) and (200) were found for the Pt/carbon catalyst at the low angle region, whereas a weak peak corresponding to Ru(101) was detected for Ru/carbon. As for the composite Ru-Pt/carbon catalyst, the overlapped peaks of Pt(111), Pt(200), and Ru(101) were prevented from resolution by broadness, but crystal growth as metal was revealed from the other peaks of Pt(311) and (220). Since the peak broadness caused difficulties in accurate determination of lattice spacings, it still remains undetermined whether bimetallic particles[7] or individual metal crystallites were formed. Crystallite sizes were found to be as small as 1.7, 1.5, and 2.0 nm for the Pt/carbon, Ru/carbon, and Ru-Pt/carbon catalysts, respectively, which would be requisite for high catalytic activities.

Synergy accomplished by the composite Ru-Pt/carbon catalyst is important for improving the low-temperature catalysis, as it is adoptable to the chemical heat pump system.

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