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COLLOIDAL NOBLE METAL CATALYSTS SUPPORTED ON INORGANIC CARRIERS

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Hydrosols of rhodium, palladium, and platinum were prepared by the $NaBH_4$-reduction of the corresponding metal salts in aqueous solution without using protective agents. Colloidal metals in the hydrosols were effectively adsorbed on inorganic carriers such as $Mg(OH)_2$, to give highly active catalysts for olefin hydrogenation.

Supported metal catalysts are usually prepared by the fixation of metal ions on carriers through impregnation or adsorption and the following reduction to metal particles on the surface of the carriers. On the other hand, the reduction of metal ions in solutions produces various sol-type catalysts consisting of colloidal metals.1) Certain colloidal metals tend to be adsorbed on inorganic substances like minerals.2) Therefore, supported catalysts may be prepared from colloidal metals using inorganic substances as a carrier. Actually colloidal nickel boride formed by the $NaBH_4$-reduction of nickel(II) salts in ethanol was immobilized on $Mg(OH)_2$ or $CaCO_3$ and gave active catalysts.3) Now we wish to report on highly active catalysts prepared from colloidal noble metals in hydrosols.

Typical procedures of catalyst preparation are as follows. An aqueous solution (5 ml) of $NaBH_4$ (200 µmol) was added to an aqueous solution (95 ml) of $RhCl_3 \cdot 3H_2O$ (50 µmol) under vigorous stirring. A rhodium hydrosol was thus obtained as a dark brown transparent liquid. The hydrosol was then added to $Mg(OH)_2$ powder (500 mg) suspended in water (50 ml). Stirring the suspension for 15 min gave a colorless aqueous phase and a gray-colored sediment which was filtered, washed with ethanol, and dried under reduced pressure to give a colloidal rhodium catalyst supported on $Mg(OH)_2$ ($Rh/Mg(OH)_2$). In a similar manner, $PdCl_2$ (dissolved in hydrochloric acid of 5 times molar quantity) and $H_2PtCl_6 \cdot 6H_2O$ were also reduced with $NaBH_4$ to form hydrosols which gave gray-colored supported catalysts, $Pd/Mg(OH)_2$ and $Pt/Mg(OH)_2$, respectively. Since $H_2PtCl_6 \cdot 6H_2O$ was somewhat hard to be reduced, it required more than 1 h to complete the formation of the hydrosol. Many other water-insoluble substances, including $CaCO_3$, $Al(OH)_3$, and ZrO_2, were applicable for a carrier.

$Rh/Mg(OH)_2$ was observed by Hitachi Model H-700 Electron Microscope. An electron micrograph in Fig. 1 indicates that rhodium particles aggregated to some extent are located on $Mg(OH)_2$ surface.

Hydrogenation of olefins was carried out at 30°C under atmospheric hydrogen pressure in a 50-ml flask connected to a buret. Supported catalyst (containing 0.5-2 µg-atom metal) was placed into the flask which was then flushed with

Fig. 1. Electron micrograph of $Rh/Mg(OH)_2$ (x 21000).

Table 1. Hydrogenation of olefins by supported rhodium and palladium catalysts

Olefin	Initial rate (mol/s·g-atom metal)[a]			
	$Rh/Mg(OH)_2$	Rh/C[b]	$Pd/Mg(OH)_2$	Pd/C[b]
1-Hexene	1.90(1)	2.12(1)	1.41(1)	0.23(2)
Cyclohexene	1.02(1)	1.66(1)	0.29(1)	0.07(2)
Styrene	0.31(1)	0.74(2)	5.88(0.5)	1.14(1)
α-Methylstyrene	0.03(1)	0.27(2)	6.19(0.5)	0.70(2)

a) The ammount of Rh or Pd (μg-atom) is designated in parentheses. b) Commercial 5% Rh or Pd catalyst supported on active charcoal.

hydrogen. Ethanol (20 ml) was poured into the flask and stirred for 1 h for its saturation with hydrogen. Liquid olefin (250 μmol) was then added with a microsyringe, and at that time hydrogenation started. The time course of the volume of uptaken hydrogen was measured.

Table 1 shows the initial rate of hydrogenation by $Rh/Mg(OH)_2$ and $Pd/Mg(OH)_2$, compared with those by commercial catalysts supported on active charcoal. $Rh/Mg(OH)_2$ is somewhat less active than Rh/C as a hydrogenation catalyst. The difference in activity between the two catalysts is large for styrenes. On the contrary, $Pd/Mg(OH)_2$ exhibits a much higher activity than Pd/C, especially for the styrene compounds.

References

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