JOURNAL OF CATALYSIS **83,** 477–479 (1983)

High Dispersion Platinum Catalyst by RF Sputtering

The development of experimental procedures for the preparation of highly dispersed metal catalysts has been spurred by (1) the observation of significant changes in catalytic reactivity and selectivity for very small crystallites (*1–4*) and (2) the recognition of metal/support interactions with decreasing crystallite size (*5*). For preparation of high-dispersion metal catalysts a number of techniques have been employed, including the use of supports impregnated with organometallic cluster compounds (*6*), metal complexes anchored by chemical reaction with the support (*7*), and metal ion exchanged zeolites (*8*). In addition, several metal-deposition procedures have been tried to produce high dispersion catalysts. One of these is ion implantation (*9, 10*), another utilizes metal sputtering, which by contrast with ion implantation does not cause as deep a penetration of the metal into the support (*10–13*).

In the present study we examined the catalytic properties of platinum sputtered onto powdered alumina. The degree of crystallite dispersion was derived from CO adsorption measurements and from the product distribution of methylcyclopentane (MCP) hydrogenolysis. It has been found (*14*) that a low Pt dispersion (crystallite diameter >100 Å) favors the formation of 2- and 3-methylpentane, with $n\text{-}C_6H_{14}/3\text{-MP} < 0.5$. Highly dispersed Pt (crystallite diameter <30 Å) is less selective, with $n\text{-}C_6H_{14}/3\text{-MP} > 1.3$ (Fig. 1).

Our catalyst was prepared by placing powdered alumina support (100 μm diameter) (chi-Al_2O_3 calcined at 673 K for 1.5 hr, BET/N_2 surface area of 110 m^2/g) onto the cone of a loud speaker (12.5 cm in diameter) vibrating at 450 Hz, thereby causing significant mechanical agitation and mixing to the powdered sample during the sputtering process (*12*). The Pt target was located at a distance of about 18 cm from the powder. Platinum sputtering was carried out in the presence of argon (1.5 Pa). The amount of Pt deposited onto the support by sputtering was determined by atomic absorption spectroscopy of the metal, which was removed from a known mass of sample by dissolution in aqua regia. A number of catalyst samples were prepared at different sputtering rates, expressed in terms of RF power applied and exposure times (Table 1). Aliquots of these samples were reduced in flowing $H_2(10^5$ Pa) at 573 K for 2 hr and exposed to flowing He at 573 K for 3 hr preceding an adsorption measurement *in situ* with CO at 296 K.

The metal surface site density was derived from the CO adsorption measurements. The results indicated that the ratio of the number of CO molecules adsorbed

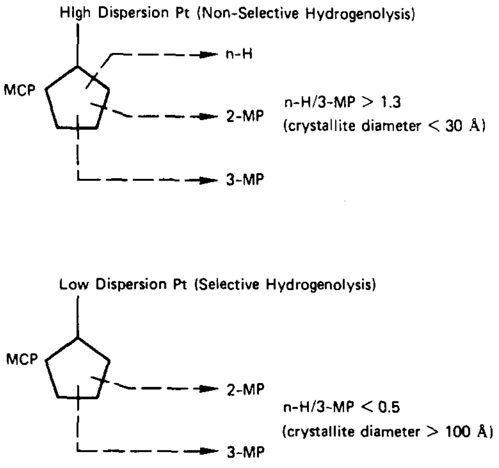

FIG. 1. Effect of Pt crystallite diameter on hydrogenolysis of methylcyclopentane. mcp, Methylcyclopentane; *n*-H, *n*-hexane; 2-mp, 2-methylpentane; 3-mp, 3-methylpentane. From Ref. (*14*).

0021-9517/83 $3.00

TABLE 1

CO Adsorption on Sputtered Catalysts

Sputtering conditions		Pt wt%[a]	CO_{irr}/Pt[b]
RF power (W)	Time (min)		
50	10	4.9×10^{-3}	0.96
50	30	1.0×10^{-2}	1.14
100	31	1.3×10^{-2}	0.60
100	50	1.9×10^{-2}	1.09

[a] By atomic absorption analysis.

[b] The amount of irreversible adsorption was obtained by extrapolation to infinite pressure of CO.

irreversibly at saturation coverage to the total number of Pt atoms in the sample was found to be close to unity (Table 1). From the amount of CO adsorbed we estimate an average Pt crystallic diameter <10 Å. In one case (100 W, 30 min) we observed CO/Pt = 0.6, corresponding to an average particle diameter of 20 Å.

Hydrogenolysis of methylcyclopentane was studied by the pulse microreactor technique (*14*) using a gas chromatograph equipped with a squalane column and a hydrogen carrier flow of 30 ml/min. Pulses of methylcyclopentane (4.7 μmole) were injected into the reactor. For each of the catalyst samples used we observed nonselective skeletal isomerization to 2-methylpentane, 3-methylpentane, and *n*-hexane (Table 2). This product pattern with $n\text{-}C_6H_{14}/3\text{-MP} \geq 1.6$ is characteristic of highly dispersed platinum (*14*) and platinum crystallite diameters of less than 25 Å. The results indicate that Pt deposition by RF sputtering provides a useful procedure for the preparation of highly dispersed metal catalysts without the introduction of foreign ions and solvents as encountered in conventional wet impregnation with metal-salt solutions.

TABLE 2

Hydrogenolysis of Methylcyclopentane[a]

Sputtering condition	50 W, 10 min		100 W, 50 min	
Reaction temperature (K)	623	648	598	623
Conversion of MCP (vol%)	5.7	16.1	3.8	21.5
Products (vol%)				
2-MP	47	42	53	36
3-MP	20	22	16	20
n-H	33	36	31	44
n-H/3MP	1.7	1.6	1.9	2.2

[a] Reaction conditions: pulse microreactor: mpc amount injected = 4.7 μmole; MCP, methylcyclopentane; 2-MP, 2-methylpentane; 3-MP, 3-methylpentane; *n*-H, *n*-hexane.

ACKNOWLEDGMENTS

The authors thank B. J. Wood, G. D. Craig, D. R. Sheridan, J. H. Hunt, and C. L. Witham for stimulating discussion and assistance with the experiments.

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Received January 31, 1983; revised May 6, 1983