JOURNAL OF CATALYSIS 85, 530–535 (1984)

The Hydrogenolysis of Methylcyclopentane on Platinum Model Catalysts

II. Particle Size Effect on Pt/SiO_2 Catalysts Due to Adlineation of Platinum and Silica

The hydrogenolysis of methylcyclopentane (MCP) on supported platinum catalysts has been investigated by many authors (*1–9*), and is known to be structure sensitive. Recently (*2*) we proposed that a reaction occurring at the phase boundary platinum/support can contribute to that structure sensitivity, when the selectivity of this reaction differs from that of the overall reaction. In particular, it was assumed that the MCP-hydrogenolysis yields only 2-methylpentane (2-MP) and 3-methylpentane (3-MP), when MCP reacts on the bulk platinum surface, while the formation of *n*-hexane (*n*-H) is enabled by adlining sites of platinum and alumina. This explains why the formation of *n*-H becomes more important when the platinum particle size decreases, i.e., the ratio of phase boundary region to platinum surface increases.

Against the validity of this concept of adlineation it may be argued that the formation of *n*-H has been observed on unsupported platinum although to a small extent. However, on films (*3*) and foils (*4*) of platinum as well on platinum black (*5*), phase boundaries may exist between the metal and any oxides formed at the surface by diffusion of impurities like Ca, Mg, Si, and Al from the bulk to the surface as was described recently (*10, 11*).

In the adlineation mechanism the kind of the support used could influence the extent of the particle size effect. However, most of the work on MCP hydrogenolysis has been performed with alumina-supported platinum and only few data are available for other supports like silica (*5, 7*). Therefore the first aim of this work was to perform experiments on Pt/SiO_2 catalysts to verify the demanding character of MCP hydrogenolysis also with the silica support. Furthermore we tried to prove the applicability of the concept of adlineation by experiments on Pt/SiO_2 model catalysts by systematically varying the ratio of the Pt/SiO_2 phase boundary to the Pt surface area without changing the size of the platinum particles.

The silica supports for the model catalysts were prepared by reactive evaporation of SiO in an oxygen atmosphere (1.3×10^{-2} Pa) onto thin Al foils (Goodfellow, 12.5 μm thick). The thickness of the deposited SiO_2 film (~30 nm) was controlled by a quartz oscillator. Simultaneously with the preparation of the catalyst, specimens for electron microscopic inspection were prepared by depositing the SiO_2 film onto carbon-coated gold grids. The foils and the grids were then heated in air at 770 K to ensure the complete oxidation of the silica films. By this treatment the carbon layers on the TEM grids were burned off, and self-supporting silica films remained on the grids.

Platinum (Goodfellow 99.99%) was then evaporated on these supports at 10^{-3} Pa pressure with a deposition rate of about 5×10^{-3} nm/s up to a mean thickness of 0.3 and 1.5 nm, respectively, to obtain both low and high dispersed catalysts (*8*). Stable particle sizes were achieved by heating catalysts and specimens in air at 770 K before they were inserted into the reactor for determining the catalytic behavior.

Figure 1a shows the micrograph of a low

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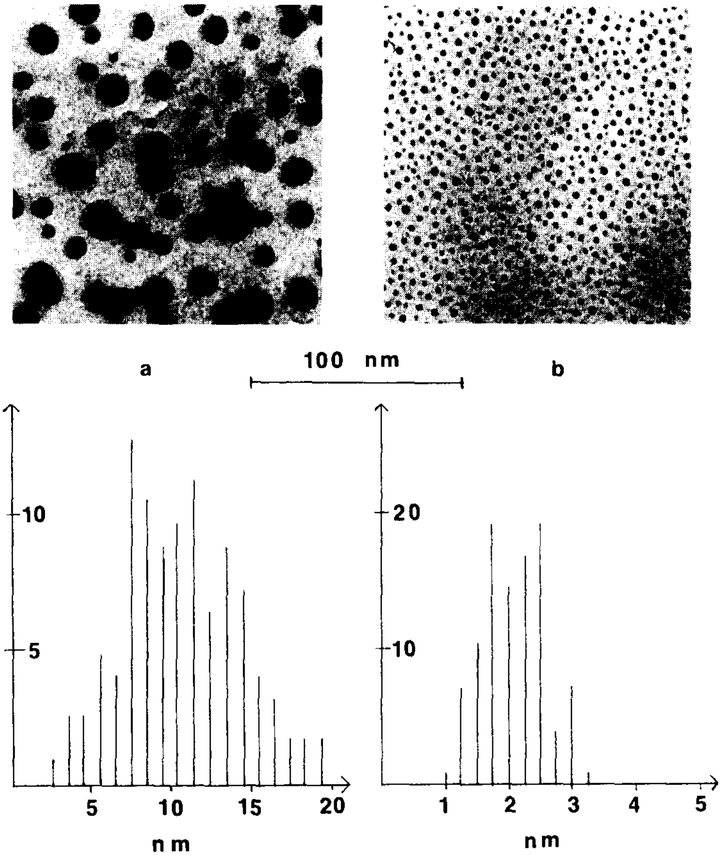

FIG. 1. Micrograph (magnified 400,000 : 1) and particle size distribution (% fraction vs particle size) of Pt/SiO_2 model catalysts; (a) 1.5 nm mean thickness of Pt, (b) 0.3 nm mean thickness of Pt.

dispersed catalyst (1.5 nm Pt deposited) and the corresponding particle size distribution. The mean size of the platinum particles is 10.4 nm and the particle density 3.0 $\times 10^{11}$ cm^{-2}. As the appearance of the particles is rather rounded, the habit of the surely polyhedral particles can be approximately described by a spherical geometry. Given the mass of the deposited platinum, the particle size distribution and the particle density, the height of the resulting calottes of spheres has been evaluated to be 6.9 nm, i.e., 66% of the diameter. Hence the particles are distinctly higher than half spheres.

From the micrographs of the higher dispersed catalyst (Fig. 1b) the particle size distribution has also been evaluated to calculate the mean size of the platinum particles. However, particles smaller than 1 nm can hardly be distinguished in the EM, and therefore the evaluated mean particle size of 2.1 nm may be somewhat too large, and the value of particle density (3×10^{12} cm^{-2}) too low. Therefore the calculation of the height of the particles has been omitted.

Besides these model catalysts the well characterized Euro-Pt 1 catalyst (6.3% Pt on SiO_2, $\bar{d}$ = 1.7 nm, Johnson Matthey Co.) (*12*) was used as a standard sample in order to prove whether the model catalysts behave like the conventional supported catalysts.

The apparatus used to measure the conversion and the product distribution of the MCP hydrogenolysis was a recirculating system that provided the long contact times necessary because of the low catalyst area employed (~170 cm^2). This apparatus has been described already (*1*). The catalysts were pretreated in oxygen at 670 K and then reduced in hydrogen at 520 K, the hydrogen pressure was about 940 mbar, the partial pressure of MCP about 5 mbar. A small amount of reaction gas (1 cm^3) was withdrawn for GC-analysis at reaction times ranging from 5 to 60 min.

The main products of the hydrogenolysis of MCP were 2-methylpentane, 3-methylpentane, and *n*-hexane. The proportion of these three products stayed constant during the reaction time, and the content of lower hydrocarbons was always below 5% of the conversion. This indicates that interfering secondary reactions like isomerization and hydrocracking occur only to a minor extent probably due to the low reaction temperature (520 K).

The results given in Table 1 show that the selectivity of the MCP hydrogenolysis depends on the particle size in the similar way as was established for Pt/Al_2O_3 catalysts. The proportion of *n*-H increases at the expense of 2-MP and 3-MP as the mean size of the platinum particles decreases from 10 to 2 nm. Furthermore, the conventionally prepared Euro-Pt catalyst fits well into the series of model catalysts. This justifies the use of model catalysts to draw conclusions as to the behavior of supported catalysts at least for the hydrogenolysis of MCP on platinum/silica.

In a previous paper (*1*) we could demonstrate that the selectivity of the MCP hydrogenolysis on low-dispersed Pt/Al_2O_3 model catalysts is shifted to an enhanced *n*-H proportion, if the platinum particles are covered with a thin layer of alumina, thereby enhancing the length of the Pt/Al_2O_3 phase boundary in relation to the platinum surface area. In order to prove whether the platinum/silica phase boundary can also contribute to the particle size effect of the MCP hydrogenolysis, we performed similar experiments with covered platinum/silica model catalysts.

After heating in air at 770 K the catalyst was covered with a thin film of silica (~0.4 nm thickness) by reactive evaporation of SiO. Because of the geometry of the particles only the surface exposed to the evaporating beam was covered by the SiO_2 layer, while the lower part of the particles was shadowed from the beam. After the catalyst was inserted into the reactor it was heated in oxygen at 520 K and then reduced at the same temperature. Indeed a small increase of the *n*-H proportion was observed with this covered catalyst (Table 2), but the shift was much smaller than the one obtained with the Pt/Al_2O_3 catalysts (*1*). Contrary to the results with Pt/Al_2O_3, the rate of reaction remained approximately the same as before. At least the trend of the selectivity shift agrees with the mechanism proposed by us, but the extent of the shift is certainly not convincing. Since the rate of reaction was hardly changed by the coverage with silica, we suspected that the cover layer might have been removed during the pretreatment. However, the alumina cover layer was

TABLE 1

MCP Hydrogenolysis on Pt/SiO_2 Catalysts at 520 K

Catalyst	Mean Pt thickness (nm)	Mean particle size (nm)	Turnover number (s^{-1})	Product distribution		
				% *n*-H	% 2-MP	% 3-MP
Euro-Pt	0.0017[a]	1.7	0.02	44	38	18
Model	0.3	2.1	0.02	35	45	20
Model	1.5	10.4	0.01	12	61	27

[a] Calculated from the Pt content and the BET surface.

TABLE 2

MCP Hydrogenolysis on Bare and Covered Pt/SiO_2 Model Catalysts at 520 K

Bare catalyst				Covered catalyst				
Mean Pt thickness (nm)	Product distribution			SiO_2 thickness (nm)	% Activity retained	Product distribution		
	n-H	2-MP	3-MP			*n*-H	2-MP	3-MP
1.5	12	61	27	0.5	100	15	60	25
2.0	11	60	29	0.4	100	13	59	28
1.5	11	63	26	20	0			
					26[a]	9	66	25

[a] After heating in oxygen at 670 K.

found to be stable at 520 K (*1*), but uncovering of the particles was observed by a hydrogen treatment at 670 K. Silica is known to have a higher mobility than alumina. The pore structure of silica is reported to collapse at about 1100 K, (*13*) while alumina is stable at this temperature, and the formation of a silica skin on metal particles (*14*) has limited the use of silica-supported catalysts.

In order to prove the stability of the silica cover layer further experiments were performed. TEM specimens of a low-dispersed catalyst were covered by a silica layer of 0.4 nm thickness. These specimens and blank samples without cover layer were then treated together in oxygen and afterward in hydrogen at 520 K. Then the specimens were covered by an additional thin film of platinum (0.3 nm mean thickness) and after that again heated in hydrogen up to 520 K to enable the platinum to incorporate, if it has impinged on a bare platinum surface, or to nucleate, if the platinum is deposited onto the support layer.

The micrographs obtained from these specimens show the small particles originating from the second Pt deposition between the large Pt particles of the original model catalyst. On top of the catalyst particles of the blank sample (Fig. 2a) no such small particles are seen, since the platinum atoms impinging on the bare platinum particles are incorporated into the platinum lattice. On the other hand the micrograph of the silica-supported catalyst (Fig. 2b) shows small clusters originating from the second Pt deposition only on top of a few of the original platinum particles. For comparison Fig. 2c shows the micrograph of an alumina-covered model catalyst prepared in the same manner. Obviously, the alumina layer withstood the thermal treatment and hence the platinum from the second deposition had to form new clusters on top of nearly all of the original platinum particles. However, the silica cover layer has been disintegrated from most of the platinum particles by the treatment in oxygen and hydrogen at 520 K. This result explains indeed why the selectivity of the MCP hydrogenolysis on the silica-covered catalyst was shifted only to a small extent to the production of more *n*-hexane, which was at least distinctly greater than the experimental error. Considering the low stability of the silica cover layer, we believe that the small change in selectivity obtained in these experiments demonstrates, that the Pt/SiO_2 phase boundary behaves similar to the Pt/Al_2O_3 phase boundary (*1*).

The result of a further experiment (Table 2) may illustrate the high mobility of silica even at moderate temperatures. A low-dispersed model catalyst ($\bar{d} \sim 10$ nm) has been covered by a 20-nm-thick layer of SiO_2 hence covering up all the platinum particles completely. After heating in hydrogen at

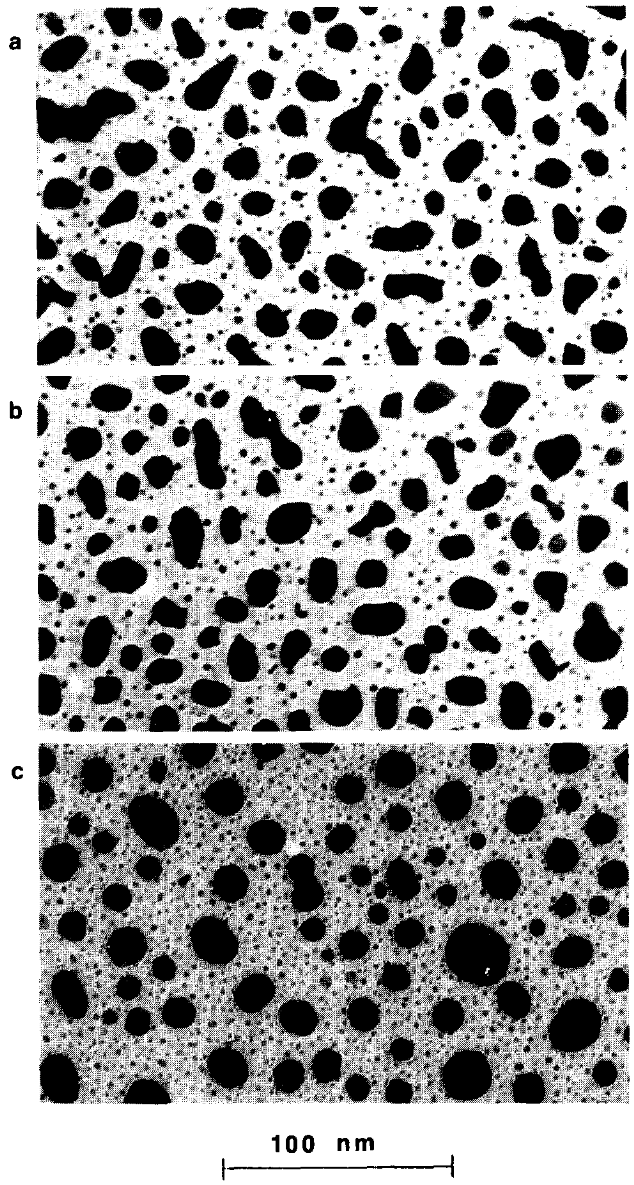

FIG. 2. Micrograph (magnified 400,000 : 1) of Pt model catalysts covered by 0.3 nm of Pt and heated in hydrogen at 520 K; (a) 20 nm SiO_2 + 2.0 nm Pt ("bare catalyst"), (b) 20 nm SiO_2 + 2.0 nm Pt + 0.3 nm SiO_2 ("SiO_2-covered catalyst"), (c) 20 nm Al_2O_3 + 2.0 nm Pt + 0.3 nm Al_2O_3 ("Al_2O_3-covered catalyst").

520 K no catalytic activity was found with this catalyst. However, heating in oxygen at 670 K followed by reduction at 520 K could reactivate the catalyst to about 25% of the initial activity. In this case, the onset of catalytic activity served as a detector of platinum appearing at the surface. Obviously the platinum has been exposed by the treatment at 670 K due to the mobility of silica. The results of other authors (*15–17*), showing that silica-supported metals loose their activity by heating at temperatures higher than 670 K can also be explained by the assumption of encapsulation of the

metal particles in the silica support due to the high mobility of silica at these temperatures. Perhaps changes in the surface and interfacial energies of platinum and silica by the treatment in oxygen or hydrogen, respectively, may cause the encapsulation or the excavation of the platinum particles in the silica.

The observed high mobility of silica could explain some of the results reported in the literature concerned with the strong metal support interaction (SMSI) mechanism. In view of this problem a similar study is being undertaken with platinum on titania model catalysts.

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Received March 16, 1983