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The Influence of Particle Size and Support on the Catalytic Properties of Rhodium for Hydrogenolysis of Hexanes and Methylcyclopentane

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The catalytic properties of rhodium for the hydrogenolysis of C_6 hydrocarbons have been investigated. Rhodium preferentially cleaves bisecondary and primary–secondary carbon–carbon bonds. Primary–tertiary C–C bonds react much more slowly. Methylcyclopentane (MCP) is converted to methyl-2-pentane, methyl-3-pentane, and *n*-hexane at temperatures lower than 503 K. The selectivity to *n*-hexane is low (10%) but measurable on well-dispersed Rh/Al_2O_3 catalysts and decreases when the dispersion decreases. Rh/SiO_2 catalysts have a low selectivity for the formation of *n*-hexane whatever the dispersion. The specific activity for MCP conversion changes as a function of the dispersion of rhodium and of the support: small rhodium particles are more active than large particles when the support is silica, but the reverse is true on alumina. These changes of activity are consistent with the results reported for C_2H_6 hydrogenolysis on Rh/SiO_2 and for C_5H_{10} conversion on Rh/Al_2O_3. The variations of the catalytic properties for hydrogenolysis may be interpreted as due to the modification of the structure of the small rhodium particles observed on silica.

INTRODUCTION

The catalytic properties of rhodium for hydrogenolysis have been very little investigated. At low temperature, rhodium in the form of a reduced metal powder catalyses mainly hydrogenolysis of *n*-heptane (*1*). On rhodium films the results are somewhat contradictory: Karpinsky and Clarke (*2*) obtained only hydrogenolysis of *n*-hexane at 550–630 K, while Peter and Clarke (*3*) observed a selectivity of 20% for benzene in the same temperature range. In a previous work (*4*) we investigated the conversion of cyclopentane on Rh/Al_2O_3-supported catalysts and reported a change of the turnover frequency for hydrogenolysis which went through a maximum at a dispersion of 25%. Yates and Sinfelt (*5*) first investigated the catalytic properties of Rh/SiO_2 in relation with the state of dispersion and reported a maximum of the specific activity for ethane hydrogenolysis around a dispersion of 50%. The shift of the maximum activity for cyclopentane could be indicative of a support effect. However, Ponec *et al.* (*6, 7*) have argued that carbon deposition has a larger effect on catalytic properties than the change of particle sizes. In order to establish the influence of dispersion on a firm basis, it was therefore necessary to use a reaction in which deactivation is minimized. This is indeed the case in the hydrogenolysis of methylcyclopentane at low temperature (*8*). This reaction presents also the interesting particularity to give information on selectivity. Gault *et al.* (*9*) have defined two types of hydrogenolysis, namely the selective hydrogenolysis which cleaves bisecondary carbon–carbon bonds, and the nonselective mechanism which affects statistically all bonds. In the case of platinum, selectivity changes with dispersion and the respective importance of the two reactions have been attributed to changes in coordination of surface atoms (*10*). Iridium catalyses a pure selective mechanism, whatever the dispersion (*11*), and this points out the

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importance of electronic factors in that reaction. The behavior of rhodium has not been investigated, and the present work tries to clarify that point. A previous paper (*12*), concerning thiophene deactivation of the hydrogenation of benzene on Rh catalysts supported by alumina and silica, concluded that the modification of the structure of the metallic particles by the support could explain the experimental results. The present data concerning the hydrogenolysis of C_6 paraffins on the same Rh catalyst are confronted with this previous work.

EXPERIMENTAL METHODS

1. Catalysts. The preparation and characterization of the Rh/Al_2O_3 catalysts have been described in detail previously (*4*); the various carriers used were "home-made" alumina (320 m^2g^{-1}) and Cataphal alumina (200 m^2g^{-1}). Rh/SiO_2 catalysts were prepared with similar procedures, using silica from different suppliers, viz., Rhône Poulenc silica (175 m^2g^{-1}) and Davison silicas (350 and 215 m^2g^{-1}). Rhodium was introduced either by ion exchange with $(Rh(NH_3)_5Cl)Cl_2$ in ammonia or by impregnation with an aqueous solution of $RhCl_3$, 3 H_2O in HCl at pH 2.

The catalysts were reduced at different temperatures. As expected, the reduction of ion exchanged samples yielded well-dispersed catalysts. The degree of sintering was controlled by the temperature of reduction and the partial pressure of water.

2. Characterization. The dispersion (*D*) of rhodium was determined by volumetry using H_2 adsorption and H_2–O_2 titration as described before (*4*). The results were checked by electron microscopy; the distri-

TABLE I

Characteristic Features of the Rhodium Catalysts Used in this Work

Catalysts			Thermal treatment			Dispersion (%)	Particle size (nm)	
Name	Metal loading (%)	Support (m^2g^{-1})	Calcined	Reduction (K)	Duration (h)	Chem.[d]	Chem.	TEM
RAl1[b]	1.0	Al_2O_3(320)	Yes	773	2	53	2.1	—
RAl2[b]	0.44	Al_2O_3(320)	Yes	823	16	87	1.3	1.7
RAl3[b]	2.35	Al_2O_3(320)	Yes	1003	16	68	1.7	—
RAl4[a,c]	1.85	Al_2O_3(320)	Yes	873	60	22	4.8	4.8
RAl5[c]	1.85	Al_2O_3(320)	Yes	823	4	30	3.8	—
RAl6[a,c]	1.85	Al_2O_3(320)	Yes	1103	48	7.5	15	15
RAl7[a,b]	1.03	Al_2O_3(200)	No	473	—	75	1.5	—
RAl8[a,b]	1.67	Al_2O_3(200)	No	973	—	50	2.3	2.5
RAl9	0.22	Al_2O_3(320)	No	773	5	55	2.1	—
RSi1[a,b]	2.00	SiO_2(175)	Yes	803	2	1.0	113	40
RSi2[b]	4.40	SiO_2(350)	No	773	—	24	4.7	—
RSi3[b]	1.0	SiO_2(350)	No	773	3	100	1.1	1.4
RSi4[b]	1.0	SiO_2(350)	No	773	16	32	3.5	5.8
RSi5[c]	2.0	SiO_2(350)	No	573	3	12	9.4	—
RSi6[b]	0.55	SiO_2(215)	No	773	—	80	1.4	1.4
RSi7[b]	0.55	SiO_2(215)	No	573	—	50	2.3	—
RSi8[b]	1.0	SiO_2(215)	No	773	3	75	1.5	—

[a] Samples have been reduced in a flow of hydrogen saturated with H_2O at 298 K.

[b] Samples were prepared by ion exchange.

[c] Samples prepared by impregnation.

[d] Chem. signifies chemical methods (H_2 adsorption and H_2–O_2 titration (*4*)).

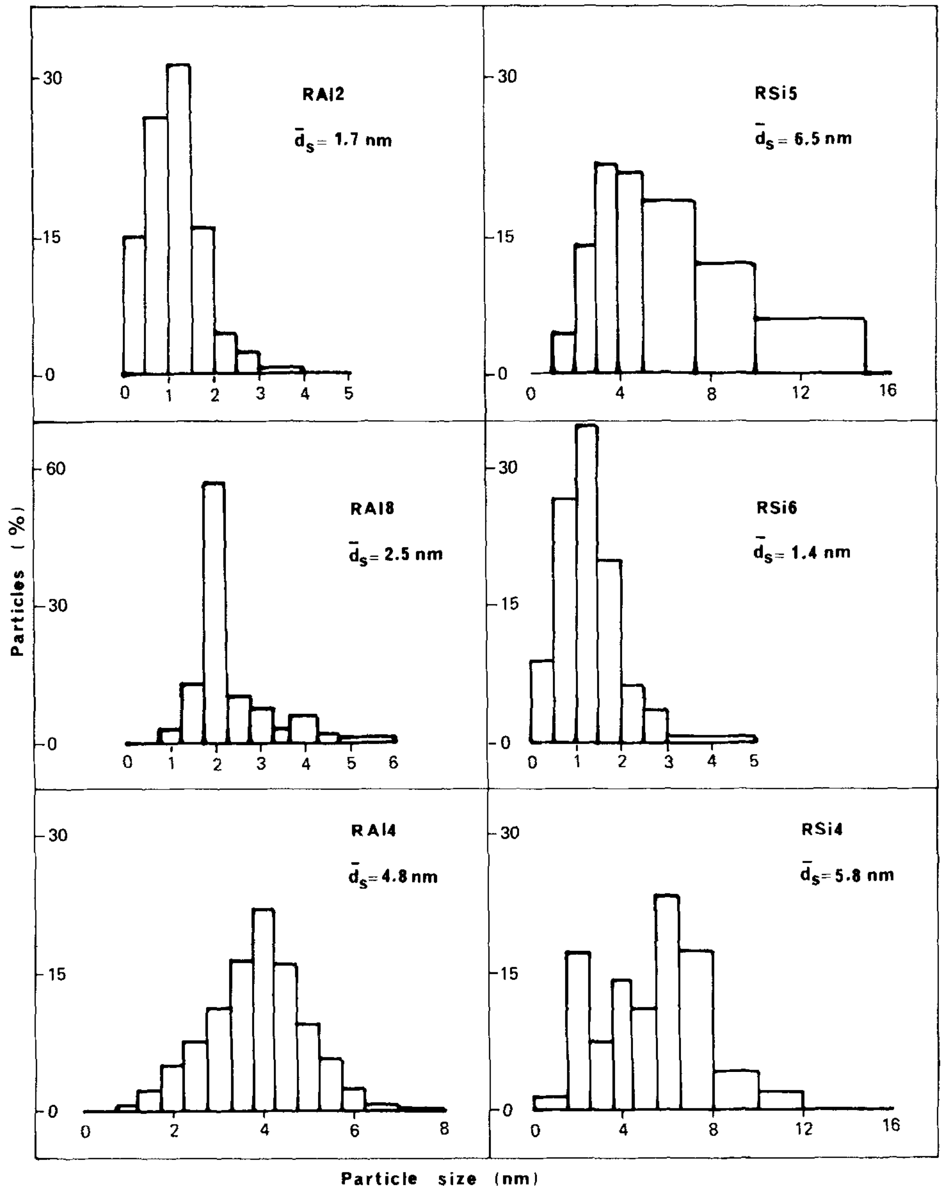

FIG. 1. Particle size distribution for different samples supported by alumina or silica.

butions of sizes of different catalysts are represented in Fig. 1. Some of the samples used in this work have been used previously for the determination of the structure of the rhodium particles by electron diffraction and weak beam techniques (*17, 18*). Their behaviour is the same as that of the other samples prepared on similar supports. Some characteristic properties of these rhodium catalysts are summarized in Table 1. We can see that in most of the cases the agreement is excellent between chemisorption and electron microscopy (TEM) for particle size determination.

3. Catalytic measurements. A conventional flow reactor was used in the differen-

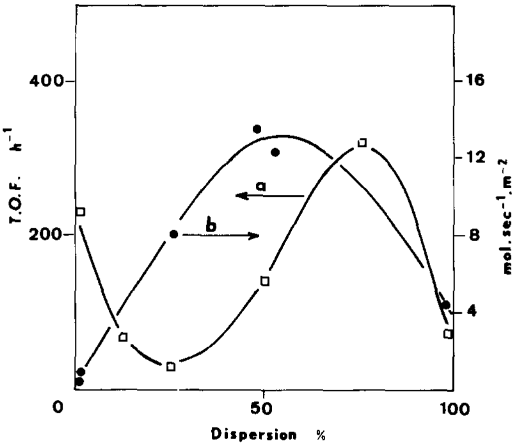

FIG. 2. Variations of the turnover frequency for MCP conversion at 496 K as a function of the dispersion of rhodium on silica (curve a). The specific activity for the hydrogenolysis of ethane at 526 K (curve b) has been reproduced from Ref. (5).

tial mode, with conversions usually less than 10%. The reactant was methyl-cyclopentane (MCP) from Fluka (uv Spectroscopy). Hydrogen was saturated with the vapor pressure of MCP at 273 K (41.2 Torr) and passed through the reactor. The products were analyzed by on-stream gas chromatography using a column (6 m × $\frac{1}{8}$ in.), packed with 10% squalane on Chromosorb W (80–100 mesh). The reaction temperature was 496 K. In these conditions, the reaction yields essentially methyl-2-pentane (2MP), methyl-3-pentane (3MP), and *n*-hexane with trace amounts of cracked products. No deactivation as a function of time was observed at this temperature. MCP has been found to have a purity of 99.3% and contains 0.5 ± 0.1% of *n*-hexane and 0.2% of cyclohexane. The blank was therefore subtracted from the reaction products and the conversion maintained at 7–10% in order to obtain a sufficient accuracy on the *n*-hexane yield.

An aliquot of the solid used for dispersion measurements was reactivated under flowing H_2 at 400°C and used for catalytic measurements. The influence of sulfur poisoning was investigated by adding thiophene (10 ppm) to MCP. Hydrogen was bubbled through the contaminated hydrocarbon and fed to the reactor.

RESULTS

The activities expressed in terms of turnover numbers, or moles of MCP converted at 496 K per surface rhodium atom, are represented in Fig. 2 for Rh/SiO_2. A clear effect of the dispersion appears. If we plot on the same figure the results previously reported by Yates and Sinfelt (5) for the specific activity of ethane hydrogenolysis on Rh/SiO_2 at 526 K, a good agreement appears in the range 10–100% dispersion. A similar behavior has been reported by Yacamán *et al.* (*18*) for hydrogenolysis of *n*-pentane on the same catalytic system.

On Rh/Al_2O_3, the results shown in Fig. 3 are in good agreement with those previously reported for cyclopentane (*4*). Compared to cyclopentane, MCP has a lower reactivity which may be partially accounted for by the fact that bisecondary C–C bonds react preferentially; MCP has only three bonds of this type against five for cyclopentane and a lower reactivity is therefore expected. The similar behavior observed with these two reactants rules out the possibility of an artefact such as poisoning by trace

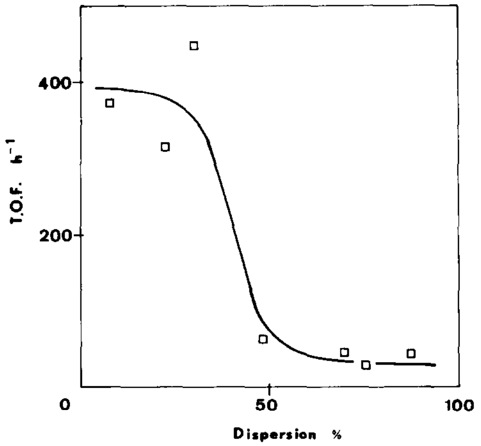

FIG. 3. Variations of the turnover frequency for the conversion of MCP at 496 K as a function of the dispersion of rhodium on alumina.

TABLE 2

Selectivities of MCP Hydrogenolysis on Rh/SiO_2 and Rh/Al_2O_3 at 496 K

Catalyst	Rh (wt. %)	Dispersion (%)	Conversion (%)	% Selectivity to		
				2MP	3MP	*n*-H
RSi3	1	100	8.8	70.5	25.6	2.6
RSi1	2	1	8.9	58.7	30.7	3
RSi7	0.55	50	15.3	69	25	1.5
			8.5	69	23.6	1.8
RSi5	2	12.5	10	64.8	28.2	3
RSi2	4.4	24	9.3	64.7	26.1	3.6
RSi6	0.55	80	58.3	65.9	27	3.2
			8	68.6	26.2	2.3
RSi4	1	32	8.3	70.4	25.3	0.7
RAl5	1.85	30	54	65.2	26.4	2.5
			7.2	66.4	26.6	2.2
RAl4	1.85	22	7.4	69.8	24.8	1.6
RAl6	1.85	7.5	9.7	65.6	25.3	2.4
RAl3	2.3	68	13.5	68.2	25.4	4.5
RAl7	1.03	75	5.7	62.5	26.2	9.3
RAl2	0.44	87	8.3	56.5	26.3	8.9

impurities contained in the reactant or carbon deposition.

Selectivities in the hydrogenolysis of MCP are reported in Table 2: the reaction yields 2MP and 3MP in a ratio close to 2/1. This represents a statistical rupture of the bisecondary C–C bonds. *n*-Hexane is produced in very small amounts, less than 3% on Rh/SiO_2, but can reach 9% on well-dispersed Rh/Al_2O_3 catalysts. The selectivity to *n*-hexane tends to decrease when the temperature increases; at temperatures higher than 573 K extensive cracking is the main reaction (93% of cracked products at 610 K) and deactivation as a function of time is observed. Apparent activation energies were determined on some samples; they are quoted in Table 3. The general trend is an increase of the activation energy when dispersion increases.

The conversion of *n*-hexane was investigated at 526 K on a few samples and the results are summarized in Table 4. In that case all bonds are broken as evidenced by the presence, at low conversion, of C_1 to C_5 paraffins. The selectivity to CH_4 is greater

TABLE 3

Apparent Activation Energies

Sample	Rh (wt. %)	Dispersion (%)	E_A (kcal mol^{-1}) in formation of		
			2MP	3MP	*n*-H
RSi5	2	12	15.7 ± 0.7	17 ± 1	12 ± 2
RSi6	0.55	80	17.2 ± 1.2	20.4 ± 0.8	25 ± 3
RSi3	1	100	21.8 ± 1.2	21.4 ± 1	28.6 ± 1.8
RAl4	1.85	22	14.9 ± 1.5	15.6 ± 2	—
RAl9	0.22	55	14.5 ± 1.5	17.5 ± 2.5	14.3 ± 3
RAl3	2.35	70	21 ± 1.4	24.5 ± 1.5	22.5 ± 3.5

TABLE 4

Conversion of n-Hexane at 526 K

Catalyst	Rh (wt. %)	Dispersion (%)	Conversion (%)	% Selectivities to					TOF[a] (h^{-1})
				CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	n-C_5H_{12}	
Si3	1	100	11	31.5	20.5	15.6	16.3	12.7	98.7
Si5	2	12	13	44.7	21.6	14.8	11.4	9.2	486
Al7	1.03	75	7	26.8	18.3	16	17.2	13.8	41
A15	1.85	30	9	47.1	16.3	12.2	11.1	11.1	323

[a] Turnover frequency.

on large particles whatever the support and the specific activity changes are parallel to those obtained with MCP. The selectivity for isomerisation to branched hexanes is negligible.

The results for methylpentanes are reported in Table 5. The conversion of 3MP gives a preferential rupture into methane and isopentane; thus there is cleavage of a primary–secondary carbon bond. The selectivity of isomerisation to 2MP (6–7%) is low but noticeable.

In the case of 2MP the main reaction is the formation of isopentane, but isobutane is also formed in large quantities. The selectivity to 3MP is approximately 10%. Propane is formed in negligible amounts, less than 5%. The absence of propane and n-pentane in 2MP, and of n-butane in 3MP conversion shows the reluctance of rhodium to cleave bonds implying a tertiary carbon atom.

The influence of thiophene poisoning on the conversion of methylcyclopentane is summarized in Table 6. A Pt/Al_2O_3 catalyst was also investigated for comparison at 573 K. The activity of platinum is slightly decreased by addition of thiophene, and the selectivity into the hexanes is unchanged. By contrast, in the case of rhodium, the conversion of MCP decreases on thiophene introduction but the selectivities to hexanes remain practically constant.

It may be inferred that sulfur contamination of the support would lead to the same final state of the catalyst. Therefore the variations in the selectivity of MCP hydrogenolysis are not due to selective poisoning of one particular catalytic site. Following a different approach a similar conclusion on the surface poisoning has been obtained in the hydrogenation of benzene on Rh catalysts (*12*).

DISCUSSION

The catalytic properties of rhodium for the conversion of methylcyclopentane to hexanes are intermediate between those of Pt and Ir. Rhodium cleaves preferentially bisecondary and primary–secondary C–C

TABLE 5

Conversion of Methylpentanes on Rh/Al_2O_3 at 526 K Catalyst A16

Reactant	Conversion (%)	% Selectivities						
		CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	i-C_5H_{12}	MP	n-Hexane
2MP	5	39	10.4	1.6	15.8	27.2	10	0.8
3MP	10.6	41.8	1.7	Traces	0.02	38.4	6.8	0.5

TABLE 6

Influence of Thiophene (10 ppm) on the Conversion of MCP. Temperature: 573 K for Pt and 496 K for Rh Catalysts

Catalyst	Dispersion (%)	Feed	Conversion (%)	Selectivity (%)		
				3MP	2MP	n-C_6H_{12}
1% Pt/Al_2O_3	100	Pure MCP	19	48.4	19.6	34.7
		+ thiophene (3h)[a]	17	48.5	19.0	36.6
1.85% Rh/Al_2O_3	22	Pure MCP	35.8	66	23.5	1.07
		+ thiophene (7h)[a]	14.8	66	24	1.1
1% Rh/Al_2O_3	58	Pure MCP	8.9	43	24.5	5.4
		+ thiophene (7h)[a]	2.9	44.8	27	6.5
2% Rh/SiO_2	12	Pure MCP	12	60	29.8	2.1
		+ thiophene (7h)[a]	4.7	60.2	26	2.0
1% Rh/SiO_2	100	Pure MCP	10	54	26.7	6.9
		+ thiophene (7h)[a]	2.4	54	29	5.2

[a] Time under contaminated feed.

bonds in MCP and hexanes. The reluctance for cleavage of primary–tertiary bonds appears with 2MP, 3MP, and MCP.

Some interconversion of 2MP and 3MP exists, and the selectivity for MCP hydrogenolysis to *n*-hexane is noticeable on well dispersed Rh/Al_2O_3 catalysts. In the classification proposed by Anderson (*13, 14*), these reactions, except for the formation on *n*-hexane from MCP, fall in the C_2-unit mode and are thought to proceed at a pair of iridium or platinum atoms. Hydrogenolysis of MCP to *n*-hexane, by contrast, is thought to occur at a single Pt atom.

It is remarkable that only well-dispersed Rh/Al_2O_3 catalysts give a non-negligible amount of *n*-hexane. This reaction is quite different from that obtained with Rh/SiO_2 catalysts of similar dispersion which give a quite lower selectivity.

At low dispersion, the selectivity pattern is identical for Rh/Al_2O_3 and Rh/SiO_2. It can then be concluded that the selectivity of MCP hydrogenolysis is affected by the particle size and by the support. *n*-Hexane hydrogenolysis is also sensitive to these factors as shown by the changes of selectivity for CH_4.

Turnover frequencies are also affected by the dispersion of rhodium and by the support. The results obtained here for MCP reproduce those previously reported for cyclopentane on Rh/Al_2O_3. In the present case no deactivation was noticed and carbon building on the surface, or trace impurities in the reactant, cannot introduce any artefact.

The results obtained with MCP on Rh/SiO_2 catalysts parallel those reported by Yates and Sinfelt (*5*) for the hydrogenolysis of ethane on similar catalysts. The similarity of the results obtained in quite different conditions confirms that the effect of the support on activity is not an artefact but a true physical reality.

When silica is used as support, small rhodium particles are more active than large particles but the reverse is true when alumina is used as support. The weak interaction which exists between rhodium and these carriers can therefore change the catalytic properties of the metal.

The possibility of a partial reduction of the carrier appears unlikely: the largest differences in activity and selectivity appear on those well dispersed catalysts reduced at low temperature (773 K) where such a reduction is very difficult. Moreover, it is known that strong metal–support interaction (SMSI) is very sensitive to water (*15*) and no clear difference could be found between the catalysts reduced in dry or wet atmospheres, at similar final dispersion. The possibility of SMSI was therefore discarded.

An interesting point is that the variation in turnover frequencies when changing the particle size or the support remain within a factor of 10. This suggests a modification of the surface structure of the metal (*16*). Indeed, some experimental evidence shows that small rhodium particles supported by silica have an icosahedral or decahedral structure in the range of sizes 10–25 Å (*17, 18*). This model for the particles was found to be consistent with diffraction and weak beam image data. Transition metal clusters of fivefold symmetry have been observed in other cases (*19*) and the transformation into a normal fcc lattice upon sintering was observed. From theoretical calculations it has been computed that metallic nuclei of small size are more stable in the icosahedral structure, while larger particles are more stable in the cubooctahedral form (*20*). The size corresponding to the transition is known only approximately and is in the range 20–50 Å for *particles isolated in vacuum*. For supported metals the influence of the carrier and reactants add difficulties. The interaction of rhodium with the support may be estimated by the facility of sintering: the latter occurs just above 800 K on silica, and above 1000 K on alumina (Table 1). The interaction of rhodium particles with silica is therefore weaker and it is not unexpected that these small particles may retain their icosahedral structure. The greater interaction which exists with alumina is sufficient to stabilize the normal cubooctahedral structure.

Such a crystallographic modification implies that the crystal planes exposed by the particle change and this also implies that the local density of states at the surface atoms is modified (*21*). The coordination number of the surface atoms is changed as quoted in Table 7. We can estimate roughly that for a small icosahedron, which consists mainly of edge atoms, surface rhodium atoms have a coordination of 8, as on a large cubooctahedron which exhibits mostly (100) crystal planes.

TABLE 7

Coordination Number for Surface Rhodium Atoms as a Function of the Structure

	Corner	Edge	(111) Face	(100) Face
Icosahedron	6	8	9	—
Cubooctahedron	5	7	9	8

In that interpretation, the two maxima of catalytic activities, either on Rh/Al_2O_3 or on Rh/SiO_2, could be interpreted as corresponding to the same high-coordination number of surface atoms.

It was recently reported that phosphine nickel cyclopentanes decomposed to produce cyclobutane, ethylene, or 1-butene depending on the coordination number of the complex (*22, 23*). The interesting points are that carbon–carbon bond cleavage may be obtained only when the coordination number of the complex is high, and this reaction may occur on one single metal atom, whenever the complex is formed. This points out the importance of coordination in the understanding of hydrogenolysis.

The experimental results may therefore be discussed in the light of these ideas. The variations of specific activities as a function of particle size are qualitatively correlated with the changes of coordination predicted by assuming that the structure of the metallic particle is modified by the support: on an icosahedron (case of Rh/SiO_2), it is expected that the relative number of edge atoms will go through a maximum and then decrease when the size increases. At low dispersion the transition into cubooctahedral particles induces the appearance of (100) faces, and an increase of the number of atoms which have a high coordination.

In the case of Rh/Al_2O_3 the activity increase with size reflects the increase of the number of atoms in (100) crystal planes.

The changes of selectivity appear only on well-dispersed Rh/Al_2O_3 catalysts. It may be speculated that the conversion of MCP to hexane needs a site of low coordination, which could indeed exist only on a small cubooctahedron. In the case of Pd, no particle size or support effect could be observed for the hydrogenolysis of cyclopentane (*24*). Simple crystallographic considerations cannot explain the difference, since Pd and Rh crystallize in the same system. Further work is necessary to clarify that point. However, the results obtained with rhodium, which is the unique catalyst on which these changes of structure have been evidenced, suggest that weak interactions with the support may noticeably alter the catalytic properties, including resistance to sulfur (*12*).

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REFERENCES

1. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20,** 223 (1971).

2. Karpinsky, Z., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **71,** 893 (1975).

3. Peter, A., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **72,** 1201 (1976).

4. Fuentes, S., and Figueras, F., *J. Catal.* **61,** 443 (1980).

5. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8,** 348 (1967).

6. Ponec, V., "Studies in Surface Science and Catalysis," Vol. 11, p. 63. Elsevier, Amsterdam, 1982.

7. Lankhorst, P. P., De Jongste, H. C., and Ponec, V., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 43. Elsevier, Amsterdam, 1980.

8. Del Angel, G. A., Coq, B., and Figueras, F., "Studies in Surface Science and Catalysis," Vol. 11, p. 85. Elsevier, Amsterdam, 1982.

9. Gault, F. G., Amir-Ebrahimi, V., Garin, F., Parayre, P., and Weisang, F., *Bull. Soc. Chim. Belg.* **88,** 475 (1979).

10. Gault, F. G., Garin, F., and Maire, G., *in* "Growth and Properties of Metal Clusters" (J. Bourdon, Ed.), p. 451. Elsevier, Amsterdam, 1980.

11. Weisang, F., and Gault, F., *J. Chem. Soc. Chem. Commun.* **11,** 519 (1979).

12. Del Angel, G. A., Coq, B., Figueras, F., Fuentes, S., and Gomez, R., *Nouveau J. Chim.* **7,** 173 (1983).

13. Anderson, J. R., A.C.S. Symposium "Chemical Physics of Catalysis," p. 361. Preprints, Atlanta, March 21–April 3, 1981.

14. Foger, K., and Anderson, J. R., *J. Catal.* **64,** 448 (1980).

15. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).

16. Boudart, M., "Proceedings, 6th International Congress on Catalysis, London, 1976," p. 1. The Chemical Society, London, 1977.

17. Yacaman, M. J., Romeu, D., Fuentes, S., and Dominguez, J. M., *J. Chim. Phys.* **78,** 861 (1981).

18. Yacaman, M. J., Fuentes, S., and Dominguez, J. M., *Surf. Sci.* **106,** 472 (1981).

19. Renou, A., and Gillet, M., *Thin Solid Films* **41,** 15 (1977).

20. Gordon, M. B., Cyrot-Lackmann, F., and Desjonqueres, M. C., *Surf. Sci.* **80,** 159 (1979).

21. Gordon, M. B., Cyrot-Lackmann, F., and Desjonqueres, M. C., *Surf. Sci.* **68,** 359 (1977).

22. Grubbs, R. M., Miyashita, A., Lin, M., and Burk, P. L., *J. Amer. Chem. Soc.* **99,** 3863 (1977).

23. Grubbs, R. M., and Miyashita, A., *J. Amer. Chem. Soc.* **100,** 1300 (1978).

24. Figueras, F., Fuentes, S., and Leclercq, C., *in* "Growth and Properties of Metal Clusters" (J. Bourdon, Ed.), p. 525. Elsevier, Amsterdam, 1980.