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Preparation, Structure, and Use of Platinum-Graphite in Hydrogenation Reactions

Despite numerous and most successful applications of graphite-supported highly active metals as catalysts in various reductions and hydrogenations (*1, 2*) there are conflicting reports with respect to their structure.

1. While intercalation in graphite (*3*) and distribution on graphite (*4–6*) of metals are reported to depend on the respective method of preparation, there is no unequivocal proof for different structures resulting either from intercalation of metal salts in graphite followed by reduction or from reduction of metal salts by potassium–graphite laminate (C_8K) (*1*).
2. Since intercalated iron chlorides were found to migrate spontaneously to the graphite surface (*7*) the formation of metal–graphite intercalates by reduction of metal salts adsorbed on graphite is most unlikely.
3. Despite the specific statement that "caution is required when only one analytical technique is used to characterize the (seemingly) intercalated material" (*7*), which was recently confirmed (*6*), X-ray diffraction is still considered to be the single appropriate tool to distinguish between the above types of graphite–metal combinations (*1*c).

Platinum–graphite was selected for this investigation for the following reasons: (a) The heavy platinum contrasts favorably with graphite in electron microscopy, found to be most appropriate for structural analyses of metal–graphite compounds (*6–8*). (b) "Platinum *in* graphite" (Graphimet Pt-1), prepared by reduction of "platinum(IV) chloride *in* graphite" (Graphimet $PtCl_4$-3) by diphenyllithium in tetrahydrofuran at −50°C, is commercially available (*5, 9*) for comparison with C_8K-reduced platinum(II) chloride. (c) Since the selectivity and efficiency of platinum-assisted hydrogenations depend on the material used as support (*10*) and since both palladium- and nickel-graphite are quite selective catalysts (*11*), the selectivity of platinum–graphite in hydrogenations needed to be investigated. Because of the three reducible centers in halonitrobenzenes, including activated carbon–halogen bonds, these molecules appeared well suited to this comparative study (*10*).

The methods used are described below.

General. Dimethoxyethane (DME) was distilled over $LiAlH_4$ prior to use; DME, potassium, and platinum(II) chloride were purchased from Fluka AG, Switzerland, Graphimet Pt-1 (platinum, 1% "in graphite") from Ventron–Alfa Products, FRG (*9*). Natural graphite was used in all preparations, but other qualities of graphite were found to be equally suited.

Platinum–graphite preparation. All samples of platinum–graphite were obtained by introducing $PtCl_2$ (1.0 g, 3.76 mmol) into freshly prepared suspensions of C_8K (7.60 mmol) (*1, 2*) in DME (40 ml) under argon at room temperature and refluxing the reaction mixture for 180 min. Filtration and rinsing with DME (30 ml) followed by tetrahydrofuran (50 ml) produced the catalyst used for the following hydrogenations. While the pyrophoric C_8K must be handled with care, platinum–graphite samples do not pose any hazards.

Hydrogenations. Each hydrogenation reaction was each performed in a Parr apparatus with solutions of 2 g of the respective

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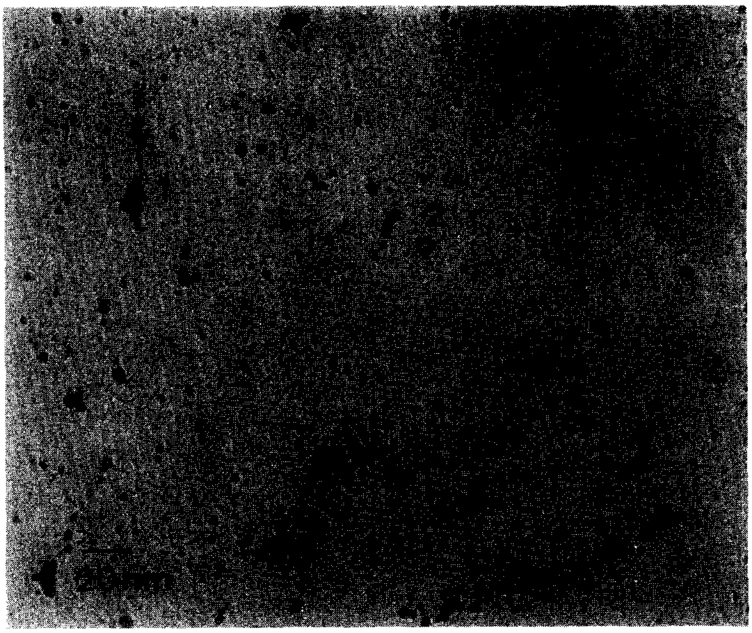


FIG. 1. TEM bright field image of Graphimet Pt-1 (9).

halonitrobenzene in absolute ethanol (50 ml) in the presence of varying amounts of the catalyst at room temperature and 50 psi (1 psi = 0.0680 atm = 6895 N m^{-2}).

Structural analyses of platinum–graphite samples. For electron microscopic (EM) investigations the specimens were dispersed by ultrasonic irradiation in acetone or THF and deposited on a holey carbon film supported by a Cu grid. Most of the images, diffraction patterns, and analytical measurements were taken of specimen areas protruding over holes in the carbon film to avoid confusion between the catalyst specimens and their support. In order to obtain representative information EDX analyses of 20 different areas in three different samples of both platinum–graphite catalysts were performed. The Philips EM 420 microscope used for this work was equipped with a LaB_6 electron source, an energy-dispersive X-ray detecting system (EDX), and an electron energy loss spectrometer (EELS) (Gatan 607) and was operated at 120 kV primary voltage. X-ray diffraction patterns of the powdery samples were recorded on a one-circle diffractometer (Siemens) employing Cu$K\alpha$ radiation.

The TEM bright field image of Graphimet Pt-1 (Fig. 1) shows uniformly and finely distributed (2- to 7-nm) platinum on graphite (5). EDX analysis of the dark area (Fig. 2a) shows platinum and traces of calcium and

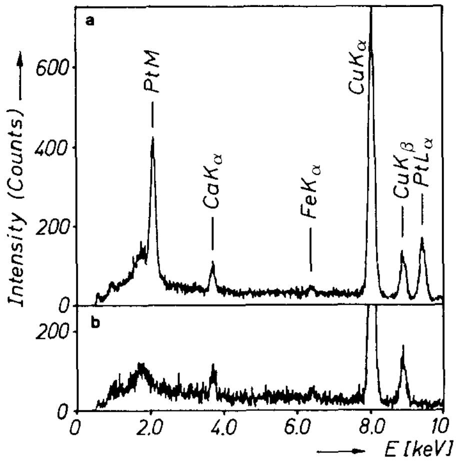


FIG. 2. EDX spectra of the Graphimet Pt-1 specimen areas shown in Fig. 1: (a) a dark particle (area 1); (b) the graphite support (area 2).

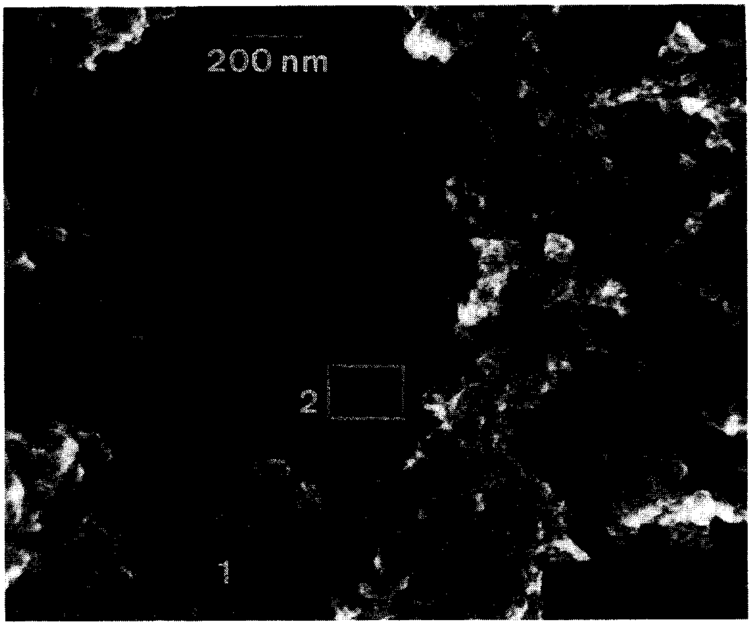


FIG. 3. Secondary electron image of platinum–graphite prepared from platinum(II) chloride by C_8K reduction.

FIG. 4. TEM bright field image of platinum–graphite obtained by C_8K reduction of platinum(II) chloride.

iron originally present in the graphite. Since no EDX platinum signals were observed in the light area (Fig. 2b), despite its low limit of detectability (~0.1 wt%) intercalation must be considered unlikely. This is supported by electron and X-ray diffractions giving no indication of alterations in the graphite lattice.

Contrary to the even distribution and low concentration of platinum in the graphimet sample, the platinum–graphite obtained by C_8K reduction of $PtCl_2$ shows a less homogeneous surface distribution with sponge-like agglomeration of small platinum crystallites (3–5 nm) (Figs. 3 and 4). Despite its much higher concentration, EDX analysis (Fig. 5) and X-ray as well as electron diffraction again show only either unaltered graphite free of platinum or graphite areas that are covered with mixtures of platinum and KCl.

From these results it must be concluded that independent of the method of preparation platinum–graphite combinations invariably consist of more or less evenly distributed platinum on graphite. Intercalation is insignificant, if it exists at all. This contrasts with conclusions drawn from other reports as to the influence of methodology on the structure (*3*).

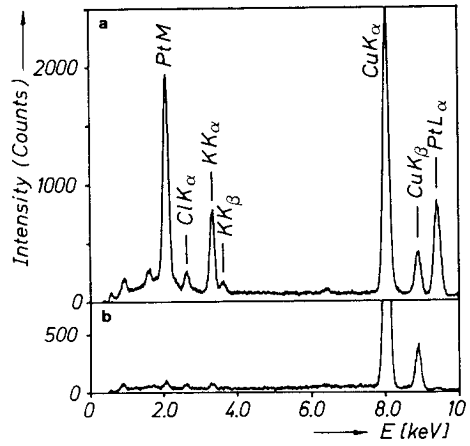
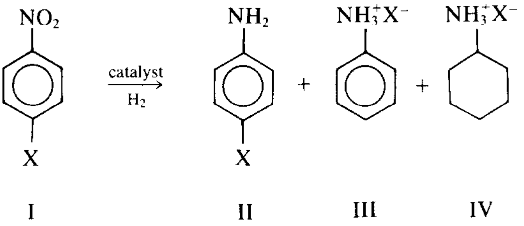


FIG. 5. Typical EDX spectra of specimen areas shown in Fig. 3 (platinum–graphite): (a) a sponge-like aggregate (area 1); (b) the graphite support (area 2).

TABLE 1

Selective Hydrogenation of *p*-Halonitrobenzenes at Room Temperature on C_8K-Derived Platinum on Graphite Catalysts



Experiment	X	Amount of Catalyst (mg)	Reaction time (min)	Isolated yield (mol %)[a]		
				I	II	IV
1	Cl	10	20	3	91	2
2	Cl	10	600	1	89	6
3	Cl	500	20	0	84	10
4	Cl	500	1200	0	80	17
5	Br	10	30	2	88	5
6	Br	500	30	0	83	9
7	Br	500	1200	0	76	18
8	I[b]	10	150	50	45	1
9	I[b]	10	500	3	91	3
10	I[b]	500	150	1	88	8
11	I[b]	500	1200	0	84	12
12	Cl[c]	500	720	3	89	5
13	Cl[c]	500	1200	1	89	6

[a] The amount of III detected was in each case less than 1%.

[b] Suspension of 2 g of *p*-iodonitrobenzene in 50 ml absolute ethanol.

[c] Catalyst: Ventron Graphimet Pt-1 (*9*), for comparison.

The hydrogenation results with the prepared catalysts are presented in Table 1 and can be summarized as follows. Even in the presence of large amounts of catalyst (500 mg) and extended hydrogenation periods the degree of dehalogenation is negligible and independent of the nature of the halogen. Hydrogenation of the aromatic ring is low. Even after repeated uses (up to 20 times) the high activity of the catalyst remained unaltered and showed no structural deterioration in AEM analysis. Both the commercially available and the C_8K-derived platinum on graphite catalysts are of comparable activity and superior to other supported platinum samples (*10*). As in numerous other highly active metal–graphite combinations (*1, 2*) the preparation of platinum on graphite by reduction of $PtCl_2$ with C_8K affords samples of totally reproducible activity.

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REFERENCES

1. For reviews, see (a) Csuk, R., Glänzer, B. I., and Fürstner, A., *Adv. Organomet. Chem.* **28,** 85 (1988); (b) Savoia, D., Trombini, C., and Umani-Ronchi, A., *Pure Appl. Chem.* **57,** 1887 (1985); (c) Setton, R., Beguin, F., and Piroelle, S., *Synth. Met.* **4,** 299 (1982).

2. For recent advances, see (a) Fürstner, A., and Weidmann, H., *Synthesis* 1071 (1987); (b) Fürstner, A., *J. Organomet. Chem.* **336,** C33 (1987); (c) Fürstner, A., and Widemann, H., *J. Organomet. Chem.* **354,** 15(1988); (d) *J. Carbohydr. Chem.* **7,** 773 (1988); (e) Fürstner, A., Csuk, R., Rohrer, C., and Widmann, H., *J. Chem. Soc. Perkin Trans. 1,* 1729 (1987).

3. (a) Braga, D., Ripamonti, A., Savoia, D., Trombini, C., and Umani-Ronchi, A., *J. Chem. Soc., Dalton Trans.,* 2026 (1979); (b) Volpin, M.E., Novikov, Y. N., Lapkina, N. D., Kasatochkin, V. I., Struchkov, Y. T., Kazakov, M. E., Stukan, R. A., Povitskij, V. A., Karminov, Y. S., and Zvarikina, A. V., *J. Amer. Chem. Soc.* **97,** 3366 (1975).

4. (a) Schäfer-Stahl, H., *J. Chem. Soc. Dalton Trans.,* 328 (1981); (b) Evans, E. L., and Thomas, J. M., *J. Solid State Chem.* **14,** 99 (1975).

5. Smith, D. J., Fisher, R. M., and Freeman, L. A., *J. Catal.* **72,** 51(1981).

6. Fürstner, A., Weidmann, H., and Hofer, F., *J. Chem. Soc. Dalton Trans.,* 2023 (1988).

7. Schlögl, R., Bowen, P., Millward, G. R., Jones, W., and Boehm, H. P., *J. Chem. Soc. Faraday Trans. 1* **79,** 1793 (1983).

8. Thomas, J. M., Millward, G. R., Davies, N. C., and Evans, E. L., *J. Chem. Soc. Dalton Trans.,* 2443 (1976).

9. Alfa Division, Ventron Corp., Sales Catalogue, p. 208 (1986); Lalancette, J. M., U.S. Patent 3,847,963 (November 12, 1974).

10. (a) Rylander, P. N., "Hydrogenation Methods." Academic Press, New York, 1985; (b) Lehmann, J., *in* "Houben–Weyl, Methoden der Organischen Chemie," (E. Müller, and O. Bayer, Eds.), Vol. 4/1c, p. 520. Thieme Verlag, Stuttgart, 1980.

11. (a) Savoia, D., Tagliavini, E., Trombini, C., and Umani-Ponchi, A., *J. Org. Chem.* **46,** 5340 (1981); (b) Savoia, D., Trombini, C., Umani-Ronchi, A., and Verardo, G., *J. Chem. Soc. Chem. Commun.,* 540 (1981).

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