
**ASYMMETRIC DISTRIBUTION OF A METAL
IN A "HETEROGENIZED HOMOGENEOUS" CATALYST*..****

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Beads of a styrene-divinylbenzene copolymer modified by dimethylaminomethyl groups (an analogue of the Amberlyst A-21 anex), were used as a support for H_2PtCl_6 in the form of its trialkylammonium salt (about 12 wt.% of Pt). A distribution of the metal in individual beads was estimated analyzing traces of Pd in 107 single beads by flameless atomic absorption spectrometry (ratio Pd : Pt = 1 : 10⁴). The distribution curve is asymmetric and fits a three-parameter, log-normal curve (Johnson S_L family of empirical distributions). The correlation coefficient between the weight of one bead and its absolute content of Pd was rather low (0.56). So, it is obvious that any biased sampling of such catalysts may cause misleading results, both in the elemental analysis and in catalytic data, especially in experiments carried out on millimole scale. A working procedure for an unbiased sampling of bead catalysts is proposed.

Selectivity is a well-known advantage of the so-called homogeneous catalysts of liquid phase reactions. In the case of expensive transition metal complexes, a practically complete recovery of these metals from products is desirable. This is not a simple task compared to heterogeneous catalysts, which can be removed easily by filtration. Both advantages, selectivity and simple recovery, can be achieved by fixing transition metal complexes on solid supports (beads, fibres, granules, grains, metallic framework, etc.). Such combined types of catalysts are known as "heterogenized homogeneous" catalysts (also anchored, attached, fixed, immobilized, insolubilized, supported, etc.). There are many reviews about this topic¹⁻²⁹.

Transition metal complexes can be fixed on solid supports by physical sorption or, more efficiently, by an ionic or covalent chemical bond, the latter being effected also through the so-called "coupling agents".

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The use of expensive platinum metal complexes necessitates checking of the metal content in the catalyst during the reaction, to reveal an eventual washing-out of the metal from supports to products. Such analyses are both time-consuming (mineralization of the sample) and "prodigal" with respect to the availability of such catalysts, *e.g.*, a rhodium catalyst with chiral phosphine coupling agents. Moreover, a random microsample of such a catalyst is not necessarily a representative one. Recently³⁰, a dimethylaminomethylated styrene-divinylbenzene anion exchanger was used for fixation of H_2PtCl_6 in the form of its trialkylammonium salt, and significant differences among several independent determinations of Pt content in random samples of that catalyst were found. Because of that we have analyzed single beads to estimate statistical distribution of the metal in that catalyst.

The aim of this work was to comment upon the asymmetric distribution of the metal in "heterogenized homogeneous" catalysts, and to suggest a working procedure for an unbiased sampling of such bead catalysts.

EXPERIMENTAL

Soluble platinum compound. A commercial solid H_2PtCl_6 (Safina Works, Vestec near Prague) contained 38.3 wt.% Cl and 38.7 wt.% Pt (molar ratio Cl : Pt = 5.45 : 1), the residue being the water of crystallization. Moreover, it contained traces of Pd in the ratio Pd : Pt = 1 : 10^4 (by flame AAS) and of Ag (Ag : Pt = 1 : 10^5 by spark emission).

Polymer support. An analogue³⁰ of the macroreticular weak base (type 3) anion exchange resin „Amberlyst” A-21 was used. Diameters of single beads were within the size of 0.3–1.0 mm. The support in the OH cycle contained about 50 wt.% of moisture and therefore all the data were dependent on the way of its drying. The nitrogen content after drying *in vacuo* at 130°C was 5.9 wt.%. Besides C, H, and N, the sample contained traces of Mg, Al, Si, and Fe (below 100 ppm by spark emission). The maximum amount of Pt which could be fixed on this support, irrespective of the excess of H_2PtCl_6 used, was³⁰ about 18 wt.% after drying *in vacuo* at 130°C.

Anchored³⁰ H_2PtCl_6 . The weighed amount of beads was introduced into an aqueous H_2PtCl_6 solution acidified with HCl to pH about 2.5. The dissolved amount of Pt corresponded to about 2/3 maximum sorption capacity of the support, *i.e.*, approx. 12 wt.% Pt, which ensured the N : Pt molar ratio equaling to about 6 : 1. After 1 h stirring, the solution turned colorless, was filtered off, and the catalyst was washed with water and dried. The IR absorption spectrum of this supported catalyst reported earlier³⁰ ($4000\text{--}250\text{ cm}^{-1}$, in KBr) proves the presence of trialkylammonium ion.

The Pt content in two independent samples of beads was determined simultaneously by two independent methods (colorimetry and atomic absorption in the air-acetylene flame) after homogenization of the samples by mineralization. The results are in Table I. At the average weight of one bead (about 100 μg) the amount of fixed Pt is about 10 μg .

Colorimetric determination of Pt. An amount of the beads (7–10 mg) was taken on air (microbalance Mettler), mineralized in a 50 ml beaker with a mixture of 2 ml HNO_3 (65% w/w) and 2 ml HClO_4 (70% w/w) on a hot plate at about 130°C until evolution of dense white fumes of perchloric acid³¹. After cooling, the covering glass and the walls of the beaker were rinsed with water and the digestion was repeated twice. The liquid residue was diluted with water to ap-

proximately 25 ml, neutralised with aqueous NaOH and heated to boiling point for about 10 to 20 min, with an addition of 5 ml of 25% solution of SnCl_2 in HCl. The cooled mixture was transferred into either 50 or 100 ml measuring flask containing 5 ml of the SnCl_2 solution. The volume was adjusted and after 20 min the absorbance of the solution was recorded in the 370–450 nm range^{32–34} ($d = 1.00$ cm, Beckman DK-2A, W-lamp). The purity of K_2PtCl_4 used as a calibration standard was tested by determining the content³⁵ of Cl and Pt. The average extinction modul of $1 \mu\text{g Pt/ml}$ at 403 nm was 0.0408 ± 0.0012 (12 measurements within the 0.3–20 $\mu\text{g Pt}$ range).

Weighing of single beads for AAS analysis. Single beads with anchored Pt were weighed on air using an electric microbalance Cahn, model Gram (Ventron Instruments Corp., California), within the 0–1 mg range with an accuracy of $\pm 1 \cdot 10^{-7}$ g. The beads did not change their weights during weighing (about 30 s) so that the content of moisture represents a systematic error.¹

Spectrometers for atomic absorption. Two single-beam spectrometers were used, one from Perkin-Elmer, model 300, with the deuterium background corrector and electrothermal atomizer HGA-70. The other one was from Varian, model AA-6, with an automatic background corrector BC-6. The electrothermal atomization of samples was carried out in a graphite cup of CRA-63. In both cases, hollow cathode Pd and Pt lamps (Atomic Spectral Lamps, Australia) were used together with argon as an inert gas in the atomizers. Pd and Pt in single beads were determined by dosing the weighed solid bead into the atomizer.

Attempt at determining Pt content in one bead by flameless AAS. The attempt was unsuccessful due to a high absolute Pt content in one bead (about 10^4 ng, Table I) since the optimum working range for, e.g., the main Pt analytical line (265.94 nm) is³⁶ 0–120 ng Pt. In the case of the less sensitive Pt line at 235.5 nm, the closed construction of HGA-70 atomizer turned out to be unsuitable for determining great amounts of Pt. Furthermore, the graphite tube exhibited a considerable memory effect after the atomization cycle, which value could not be decreased even by repeated heating to maximum temperature.

TABLE I
Quantitative Determinations of Pt Content in an "Amberlyst"-like Supported H_2PtCl_6 Catalyst

Weight of beads mg	Content of Pt, wt. %	
	colorimetry	flame AAS
8.50	12.15	11.77
7.15	13.93	13.18

TABLE II
The Experimental Conditions for Determining of Pd Traces in Excess Pt in Solid Single Beads During the Electrothermal Atomization^a

Program	Temperature, °C	Voltage V	Time s
Ashing	1 710	5.5	30 ^b
Atomization	2 600	10	15

^a PE-300; HGA-70; in argon; at 244.8 nm; spectral band width 0.7 nm; lamp current 25 mA. ^b The optimum time for fast ashing of the organic matrix preventing losses of the analyse Pd atoms.

For that reason, the metal distribution in single beads had to be tested by means of trace metals present in H_2PtCl_6 .

Non-destructive detection of traces of Pd and Ag by X-ray fluorescence spectrometry. The measurements were carried out on Tracor Northern instrument, model NS-880 (Middleton, Wisconsin, U.S.A.), equipped with a microilluminator. In the case of a single bead placed on a polystyrene foil, the focustion was time-consuming. In spite of this, the Ag and Pd signals were detected but with a low reproducibility, which made the quantitative determination impossible. In the case of simultaneous examination of a greater number of beads, the Pd signal was detected immediately but the quantitative determination was again impossible because of different geometry of the sample and the reference standard (beads vs pressed disc of $(NH_4)_2PdCl_4$; Johnson-Matthey, England).

Determination of Pd traces in a single bead by flameless AAS. Palladium was present in trace amount suitable for such a determination³⁷, i.e., about 1 ng Pd in one bead. The necessary condition that an excess of Pt by several orders of magnitude does not interfere the Pd determination by flameless AAS was verified earlier³⁸. The Pd content in single solid beads was determined by the method of calibration curve, using an aqueous $(NH_4)_2PdCl_4$ solution as a standard. The stock solution of the standard containing 1 mg Pd per 1 ml was obtained by dissolving the palladium salt in 1% (vol.) HCl, the reference solutions were obtained by diluting the stock solution with re-distilled water and adjusting HCl concentration to 0.1% (vol.). The calibrated range was 0–15 ng Pd with the relative error within 5–2%. In the analysis of single solid beads the tube was purified mechanically after each atomization of the sample and heated to maximum temperature. On using this procedure, no residual Pd signal from the preceding determination was observed. The working procedure is in Table II.

TABLE III

Parameters Characterizing the Random Sample of the Bead Catalyst

Sample size: 107 beads; the correlation coefficient between the weight of one bead and its absolute Pd content is 0.56.

Parameter	Weight of bead ^a μg	Content of Pd	
		absolute, ng	relative, wt. ppm ^b
Range of data	90.0–546.5	0.94–10.7	8.7–70.6
Mode (cell width)	113 (25)	1.3 (0.5)	13.0 (0.5)
Median	122.0	1.90	13.7
Mean	142.22	2.4255	17.6
R.m.s. deviation	± 65.47	± 1.59	± 10.7
Skewness ($\sqrt{b_1}$) ^c	3.0649	2.3284	2.5578
Kurtosis (Peakedness; b_2) ^c	15.9525	10.2185	10.1071

^a The total weight of all 107 beads is 15.26676 mg; the total Pd content is 259.5285 ng. ^b The absolute Pd content in a single bead divided by the weight of that bead. ^c For normal distributions the values of $\sqrt{b_1}$ and b_2 are equal to 0 and 3, resp.; dimensionless.

Statistical evaluation of the data from flameless AAS. All computations were done on a programmable desk-top calculator Hewlett-Packard, model HP 9830A, with appropriate programs in BASIC language.

RESULTS

The sample of 107 beads used to determine Pd traces in the anchored Pt catalyst is characterized in Table III. It is clear that for both the weight of one bead m and its absolute Pd content p the respective mode, median, and mean are different and thus these two distributions are not symmetric but skewed to the right³⁹. The correlation coefficient between the weight of one bead and the absolute Pd content in it is rather low (0.56). From the chemical point of view the sample of 107 beads does not represent a homogeneous system. Thus, a distribution of the relative content of Pd in one bead $c = p/m$ (i.e., the Pd concentration in wt. ppm) cannot be symmetric, too, as it is clear from Fig. 1 and Table III. Moreover, the "mean concentration of Pd" in one bead $\bar{c} = \bar{p}/\bar{m}$ is meaningless (17.6 ppm) since the weight of one bead was not constant but varied in a wide range (90–547 μg). Under these circumstances there is no reason to consider highest Pd contents as gross errors and to seek for their elimination from the data, as it is usual with homogeneous materials having the correlation coefficient close to 1. Similarly, the asymmetries of the distribution curves obtained cannot be considered as being due to experimental resolution³⁹.

Since we miss an unambiguous explanation of the asymmetric distribution of Pd in the beads (see Discussion), we have approximated the experimental data for the weight of one bead and for its absolute Pd content by the Johnson empirical distributions^{40,41}.

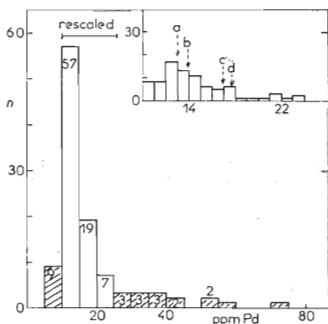


FIG. 1

A Histogram of the Relative Pd Content ("Concentration" in wt. ppm) in 107 Single Beads Indicating an Asymmetric Distribution Curve

n Number of beads; a mode; b median; c "concentration of Pd"; d mean.

It follows from the estimates of skewness and peakedness presented in Table III ($\sqrt{b_1}$ and b_2 , resp.) that an approximation can be done by using the so-called Johnson S_L family for each transformed variate ($x' = \ln(x - \varepsilon)$) bounded at lower end. This is the simplest case of a three-parameter, log-normal distribution (mean, variance, location parameter ε). Our results are collected in Table IV for the case in which the ε values are not known. The calculated ε 's are the lowerbound values of the variates, *i.e.* the minimum weight of one bead and its minimum content of Pd, and they are close to the corresponding experimental values. We further gather from Table IV that the approximation by the Johnson S_L family is fairly good because the estimates $\sqrt{b_1}$ for skewness are now practically equal to zero and b_2 for peakedness are close to 3 in each case. Thus, the assumption of normal (Gaussian) distributions of our new variables $x' = \ln(x - \varepsilon)$ is substantiated. The variances of the new variables were used to estimate the fiducial limits of the means of the transformed weight of one bead and its absolute Pd content at different significance levels.

The values of the means after the antilog-transformation are close to the median values of the original variables. Understandably, the fiducial limits after the antilog-transformation are no more symmetric in respect to the transformed means. Figs 2 and 3 summarize the changes in these fiducial limits in dependence on the size of a sample, namely on decreasing number of beads in the sample. The ratio of the transformed means of the absolute content and of the weight of one bead gives an "average"

TABLE IV
Empirical Three-Parameter Log-Normal Distributions of the Transformed Variables
Johnson S_L family; sample size: 107 beads.

Parameter	Weight of bead, μg	Abs. Pd content, ng
Skewness ($\sqrt{b_1}$)	0.0031 ^a	-0.0355 ^a
Kurtosis (b_2)	2.7726 ^a	2.7025 ^a
Location ε	85.4	0.80
Min. exp. value	90.0	0.86
Original median	122.0	1.90
Transformed mean	121.1	1.91
Fiducial limits ($n = 121$)	90%	116.3—126.3
	95%	115.4—128.0
	99%	113.8—130.4
		1.78—2.07
		1.74—2.10
		1.69—2.17

^a Dimensionless.

relative content of Pd, *i.e.*, the "average concentration" of Pd in one bead. In our case of 107 beads it is 15.7 ppm Pd, which compared to the original meaningless value of 17.6 ppm Pd gives a change by more than 10%.

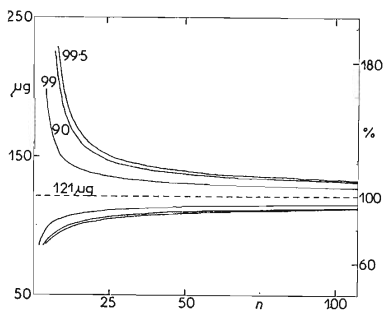


FIG. 2

The Fiducial Limits of the Average Weight of One Bead (in μg) at the 90, 99 and 99.5% Significance Levels as a Function of the Number of Beads (n) in a Sample

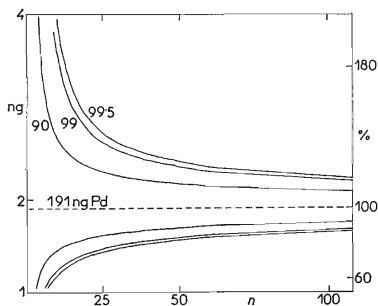


FIG. 3

The Fiducial Limits of the Average Absolute Pd Content (in ng) should be 1.91 ng in One Bead at the 90, 99 and 99.5% Significance Levels as a Function of the Number of Beads (n) in a Sample

DISCUSSION

The results presented in the preceding part prove the asymmetric distribution of Pd in the beads with the anchored Pt catalyst. We assume that the bulk metal (Pt) has the same asymmetric distribution as Pd. Moreover, we believe that the case described here is not unique but by far more frequent.

Catalytic properties of anchored complexes have been extensively studied in a number of reactions such as hydrogenation, hydrosilylation, hydroformylation, oligomerization and polymerization, including enantioselective syntheses. In some studies, attention has been paid to the effect of the type of the support on the effectiveness of a given catalyst as well as on the stereochemical course of the reaction. In the case of transition metal catalysts bound to organic polymers, the degree of cross-linking of the polymer matrix⁴² as well as the polarity of the functional groups attached to it^{43,44} have been shown to influence the performance of the catalysts by controlling the penetration of reactants into the supports. Another factor of practical importance which has been studied was the unwanted solubilization of the attached catalyst during catalyzed processes. In studies of these problems, experiments have been frequently made on millimole scale at which a non-representative sampling of the catalyst may in principle significantly affect the results.

The asymmetric distribution of Pd observed in the sample of 107 beads is presumably due to a superposition of several influencing factors: differences in the texture of individual beads introduced already during the cross-linking polymerization, a different accessibility of the functional groups ($-\text{CH}_2\text{N}(\text{CH}_3)_2$) which also need not be distributed symmetrically, *etc.* The aim of this work was not to analyse all these causes or to perform a complete statistical solution which in principle is possible. We wanted only to point out the risks involved in the studies of such systems when a larger set of experiments is needed to account for all the factors. High prices of these catalysts may lead to the reduction in the number of experiments needed and/or to the lowering of the weight of samples of these catalysts to hundreds or tens of milligrams.

For instance, let us consider the example from Table I. According to colorimetry, the contents of Pt in our catalyst are 12.15 and 13.93 wt.% Pt. In this order of events and if the samples are withdrawn during the catalysed reaction, a funny conclusion that the content of Pt increases during the reaction must be rejected. In the reversed order of the events, 13.93 and 12.15 wt.% Pt, an erroneous conclusion can be drawn — the Pt compounds is washed out into the products — which can stimulate a series of fruitless experiments how to prove a minute amount of Pt in a large volume of organic products. Third erroneous possibility is, *e.g.*, to speculate about the reliabilities of the two analytical methods used. The correct answer is that the material analyzed is remarkably heterogeneous and the random samples are non-representative.

Let us assume that the "concentration" of Pd, as the ratio of two random variables,

is another random variable with normal distribution. The fiducial limits of the arithmetical average are on Fig. 4 in dependence on the number of beads in a sample. In the case of our catalyst the conditions required are not fulfilled and the real situation will always be much worse than indicated. The reason of a wide spread of data lies in the heterogeneity of the material, not in a low reliability of the analytical methods used. Any small random sample of the bead catalyst implies a large uncertainty in the results. Consequences of such non-representative dosing of the catalyst for the reproducibility of catalytic data can easily be foreseen.

So, the use of anchored catalysts means the use of more labourious sampling procedures including sieve analysis, coning and quartering, *etc.* To minimize the above-mentioned effects of the asymmetric distribution of a metal in the bead catalysts, we suggest the following optimum procedure: a very narrow fraction of beads is sieved out. After a reaction of the soluble transition metal complex with the bead support, a materials balance is evaluated. The so-called balance concentration of the bound metal is given by the difference between the initial and final concentrations of the metal in the solution. Then, from this heterogenized catalyst 2 samples of beads are taken, each containing at least 200 beads counted off precisely⁴¹. After homogenization of the two samples by mineralization, the analytical concentration of the bound metal is determined. If these two concentrations, balance and analytical, are within prescribed limits of tolerance, these samples are the representative ones.

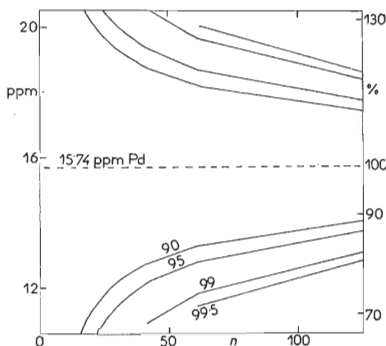


FIG. 4

The Fiducial Limits of the "Transformed Concentration" of Pd (in wt. ppm) at the Four Significance Levels as a Function of the Number of Beads (n) in a Sample

If not, the sampling must be repeated with an increased number of beads in the sample. A dosing of the catalyst should be done with the same or greater sample size. In this connection, it is noteworthy that the published experiments with anchored catalysts contain only the data about either analytical or balance concentration of the metal, never both of them. The discussed type of complex catalysts was usually described by specific terms which were listed in the Introduction. On the basis of the preceding discussion we take the adjective "heterogenized" as the most appropriate because it underlines the original meaning of the word. We can only repeat together with the well known analytical handbook:^{4,5} "The sampling of the material that is to be analyzed is almost always a matter of importance, and not infrequently it is a more important operation than the analysis itself".

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Translated by the authors (R. Ř. and J. H.).

Note added in proof. Similar asymmetric distribution curves of metallic nickel particle size in Ni-Mg catalysts (obtained by co-precipitation of the oxalates) were proved by magnetic measurements (Dreyer H.: *Z. Anorg. Allgem. Chem.* **362**, 233, 245 (1968)).