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STRUCTURE AND CATALYTIC ACTIVITY OF SURFACES

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INTRODUCTION

In the last century and actually up to World War II, the power and wealth of industrialized countries could be measured by their steel and coal mining industries. For the period which followed, this function can be ascribed to the chemical and electronical industry and the wealth of the country is very well reflected by the level of the country's agriculture. The latter is again related to the agricultural-chemical industry which as well as the manufacturing of new or currently used materials of the electronical industry is dependent on many chemical processes.

It is only a very rough estimate, but probably abt. 70% of all chemical processes used has something to do with a phenomenon called "CATALYSIS". Typical catalytic processes are: productions of sulphuric and nitric acid, ammonia synthesis, oxidation of olefines into ethylene-oxide. ammoxidation of propylene into acrolein, numerous polymerization processes and the whole production of gasoline from the crude oil is also "catalytic".

Catalysis is a kinetic phenomenon. Let us consider a hypothetic reaction of A and B giving a product P.

$$\nu_A A + \nu_B B \rightleftarrows \nu_P P \qquad (1)$$

This reaction achieves finally an equilibrium which is described by an equilibrium constant K. For a reaction at not too high pressures, K can be expressed by partial pressures

$$K = \frac{P_P^{(\nu_P)}}{P_A^{(\nu_A)} \cdot P_B^{(\nu_B)}} = \exp\left(- \frac{\Delta G^\circ}{RT} \right) \qquad (2)$$

where G° is a standard free enthalpy (a change from P_A, P_B, P_C each equal 1 bar, to the equilibrium pressures). By definition: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, being related to the enthalpy and entropy changes due to the reaction. A catalyst changes the rates $\overrightarrow{r}$ and $\overleftarrow{r}$. Since a catalyst does not participate in eq.1 (this is his definition) it does not change the thermodynamic parameters ΔG° and K. If the catalyst forms one phase with the reactants we call it a <u>homogeneous</u> catalyst, if it forms a separated phase, it's a <u>heterogeneous</u> catalyst.

In - probably - more than 90% practical cases, a heterogeneous catalyst works as follows (since now on we shall consider only the heterogeneous catalysts). The gaseous or liquid components of a catalytic reaction are first adsorbed on the solid surface and in many cases transformed into different species - by dissociation and rearrangements of certain bonds. Various adsorbed complexes interact then with each other, giving desorbable products which are observable by analytical means (gas-chromatography, mass spectrometry, etc.) in the gas or liquid phase. This is most frequently an easier way (catalytic reactions run under lower temperatures) leading to a smaller group of products (i.e. the <u>selectivity</u> is higher) and the overall reaction can be better controlled, than when the reactions run without any catalyst. Some reactions are even virtually impossible without any catalyst.

Adsorption complexes

The very essence of catalysis is thus the formation of proper adsorption complexes, and - of course - in the past all kinds of spectroscopics have been already mobilized to characterize the adsorption complexes: electronic spectra, vibrational spectra, magnetic resonances spectra, Mössbauer spectra, etc. It should not be forgotten that there are also important chemical methods to characterize the adsorbed complexes and one of them (exchange reactions) is mentioned below.

With regard to the physical methods - a short remark. When an adsorption complex is visible, by one or another spectroscopy, it does not necessarily mean that this species is an active intermediate of the catalytic reaction. It can be also a species on the end of a dead lock street. This does not mean again that an information on it is of no value at all, only - one has to think about it which species are actually monitored by the techniques used.

Let us confine in what follows to the metallic catalysts. Adsorption complexes comprise then several atoms originating from the reactant molecules and one or more atoms of the metal surface. It is to note immediately a very interesting problem: "how many metal atoms are involved directly, by forming chemical bonds, or indirectly by staying as ligands round the central coordinated site (consisting of one or more atoms), in the formation of catalytic intermediates or other adsorption complexes". Examples of information in this problem are presented below.

When more than one metal atom is involved in the formation of an adsorption complex, the structure, the geometrical arrangements of the surface, plays obviously a role. However, it is also so, when even only one single metal atom is involved, since properties of the surface atoms are also dependent on the coordinating (ligand) atoms in the nearest neighbourhood.

There are several ways how to get hold on this apsect of the formation of complexes and to study interaction of reaction components on varying structures of surfaces. We shall review here three of the techniques.

Field emission microsocpy

For some reactions valuable information can be obtained by the Field Emission Microscopy, introduced by the great German physicist E.W.Muller (1). Since this technqiue was not a subject of other courses, a short description
fig.1 of the technique, might be helpful (2)
The sharp tip (T) (50-100 nm) is in most cases formed from a single crystal and it can be easily modelled by a hemisphere cutting the single crystal. Under a high voltage, electrons tunnel into vacum and depict on the screen a projection of various crystallographic planes. A picture of this projection
ig.2 with several planes identified (by comparison with a model) is shown in fig.2.

Emission current is higher on places with lower work function Φ. Work function differences cause that the most stable planes) highest density of atoms) are dark and the changes caused by adsorption or reaction are thus most easily detected on the rough planes (due to the Smoluchowski effect they have the lowest Φ (3)). Techniques have been developed which allow to follow ΔΦ caused by adsorption or reaction, on small spots on the surface, including the dark regions (5).

Let us mention at least in brief, some results obtained by this technique (see e.g. ref.5-8). Oxygen adsorption follows an order in the reactivity of various planes which reflects the strength of the M-O chemisorption bond (M-metal). The strength is the higher, the higher the number (coordination by-) of metal atoms which can potentially surround an - O - atom (6,7). The reactivity of the M-O layer towards hydrogen follows just the oppposite order, indicating that the relation catalytic activity - chemisorption bond strengths is antipathic one. The picture becomes more complicated with a slightly more complicated molecule NO. (8); the order in activities in which NO is being dissociatively adsorbed is:

Rh(321) > Rh(331) > Rh(210) > Rh(100) > Rh(111)

(with Rh as an example).
Obviously, here play also some factors a role (electronic structure of surfaces), other than the coordination of adsorbed species.

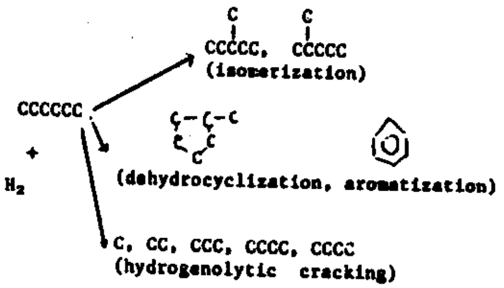
Adsorption and catalysis on single crystal planes

The development of the vacum technqiue in the fifties made another approach possible in attacking the problems of crystallographic plane specifity (crystallographically different adsorption sites are assumed to vary in parallel): the use of well defined crystallopgraphic planes cut out of single crystals. Not only the most stable lowest index planes can be prepared but also various high-index-planes, with a varying population of steps, kinks, corners, etc. In the beginning, these studies were limited to low pressures, but soon, Somorjai and his colleagues (a School which pioneered all this research) developed a technique which combines the preparation and characterization of well defined planes in the UHV chambers, with the following reactions at rather high pressures, up to several bars (9,10).

The first papers reported extreme differences in activity among various planes claiming that the flat planes are inactive at all (11). Later research did not confirm those conclusions in all details, but important differences among different crystallographic planes have been found, indeed.

fig.3 Figure 3 can serve as an illustration of the results of such studies. However, a few words on the subject, first.

Hydrocarbon reactions on Pt form a complicated network with a typical pattern of products (selectivity) for each metal. With hexane as an example:



(3)

(hydrocarbons represented by the carbon-skeletons, hydrogen atoms ommitted). A close inspection of product patterns and the use of labelled (^{13}C-,) molecules revealed (13,14), that the same products of isomerization can be formed from various adsorption complexes (involving 3 or 5 carbon atoms) or - through a consecutive reaction via the gas phase: desorption and readsorption of methyl - cyclopentane. It has been further established that there are several well distingishable mechanisms of hydrogenolytic cracking etc. As can be derived from figure 3, formation and reactivity of intermediates is related to the geometry of the adsorption sites.

Important catalysts of the reactions (reforming of naphta in the production of high octane number gasoline) modelled by scheme (3) are "bimetallics" (sometimes - alloys). The most important bimetallics are the Pt/Re, Pt/Ir and Pt/Sn (15,16) combinations and a lot of fundamental work has been also done with model alloys such as Ni/Cu, Pt/Au, Pd(Ag, Pd/Au, Ru/Cu, etc. (For review see refs. 15-19).

The importance of the surface geometric structure has been recently demonstrated again, but now with alloys. Somorjai et al. (20) studied n-hexane skeletal reaction on the Au-Pt(111) and Au-Pt(100) planes. With the first mentioned plane, isomerization rate (per Pt atom available at the start of the reaction) increases appreciably and monotonously with increasing Au content, although Au itself is inactive for this reaction, while with (100) this increase is only moderate. In contrast with it, hydrogenolysis decreases with Au increasing, with both planes. The authors conclude, that alloying of Pt with Au in the (111) fcc plane symmetry, creates sites particularly suitable for isomerization.

Hydrocarbon reactions mentioned above are examples of structure sensitive reactions. However, not all hydrocarbon reactions belong to the groups of structure sensitive reactions. Hydrogenation of C=C bonds is a much less sensitive reaction (21) and there are also some other reactions, which macroscopically monitored (i.e. by measuring the netto overall rates) manifest themselves as structure insensitive reaction. Oxidation of CO seems to be one of them (21).

Let us mention already on this place that a surprisingly low structure or particles size sensitivity (see below) of certain reactions, has raised a question whether in all cases the sensitivity (or insensitivity) established experimentally, is an intrinsic property of a reaction, or is - perhaps - induced by some side effects. For example, with a molecule of di- tertiarybutyl-acetylene (in which the triple bond C ≡ C is sterically screened oy bulky tert-butyl groups and yet its hydrogenation is particle size insensitive) a possibility has been discussed that the reacting molecule extracts a metal atom with which it reacts, out of the surface, making the original surface structure irrelevant for the running reaction (22).

How many metal atoms constitute an adsorption site?

This is by no means a purely academic question. It is a qeustion of great importance for a rational way of catalyst preparation. However, the fundamental value of an answer is of course, not negligible. The modern theory of chemical bond of various spectra, etc. of molecules like benzene started in the last century by establishing the stechiometric ratio of elements: C_6H_6, and by writing down the simplest schematic molecular structure - the Kekule form. A similar ratio $C_xH_yM_z$ comprising the surface metal atoms M, is not known for most of the adsorption complexes, what dramatically documents the real level of our knowledge on adsorption and catalysis. Needless to say that our current schematic description of "metal - adsorption complexes" bonds is probably even less correct than the Kekule's form used to be a century ago.

A few molecules form an exception (23) and more is known about them. Molecule CO is one of them. With regard to this molecule quite a detailed information on its adsorption site is available. Bradshaw and Hoffmann (24) suggested several conslusions on this subject which are now generally accepted. With Pd(111) as an example:

1) at lowest coverages θ(CO), CO occupies threefold sites and absorbs IR at about 1920 cm^{-1} ($\theta < 0.35$).

2) At higher coverages, CO can be shifted out of its optimal position into the two-fold (bridge) sites; such sites are also populated on Pd(100); CO in these sites absorb IR at 1880-200 cm^{-1}.

3) At coverages θ(CO) nearing saturation (calculating θ in surface M-atoms this happens at $\theta > 0.5$) single coordinated CO appears with $\nu =$ 2050-2100 cm^{-1}. Various structures corresponding to various LEED patterns are shown in figure 4.

Particle size effects

With only a very few exceptions (Fischer Tropsch synthesis of hydrocarbons, ammonia synthesis), the industry does not use "bulk" metals. Since catalysis is a surface phenomenon, one tries to enlarge the surface of the metal (i.e. tries to disperse it) as much as possible, until almost all metal atoms in the system are in the surfaces. Such systems must be prepared and then protected against the loss of surface area by aggregation and by sintering. To this end the metals are dispersed over a surface of "supports", such as SiO_2, Al_2O_3 and other oxides or other compounds. One can prepare metals with D, dispersion (= number of metal atoms in the surface/number of all metal atoms) nearing unity. The question immediately raises - by increasing dispersion - do we only change the size of particles, keeping the metal chemically the same or - in other words - do the metal atoms of small particles react in the same way as those of the bulk metals? The answer is - no (for review see 16,26).

Many reactions are particle size sensitive, the hydrocarbon skeletal reactions among them (16). Although the question of the particle size sensitivity is on the first glance rather straitforward, it took quite a long time to learn to appreciate the particle size effects and to aknowledge in proper proportions all side effects of it.

It is a simple exercise to imagine how small particles grow, going from 1 to 2, 3, 4 and more and more metal atoms (27). By involving rules minimizing the energy (maximizing the bonds and "bond-energy") one can derive the probable shapes of the smallest possible particles. This simple procedure has lead to several very interesting results (27).

Formation of a metal in a fcc structure follows probably this sequence. Three atoms form obviously a triangle, four atoms - a tertrahedron. Then, the straitforward growth of fcc frame is interrupted and five atoms form a trigonal bipyramid. This grows further into tripyramid and seven atoms - pentagonal bipyramid. Further growth follows the line to 13 atom icosahedron, when coming atoms are regularly placed above the existing faces of the bipyramid. In the same way the "complete" bodies are formed as: 33 atom dodecahedron (made from pentagonal planes) and 55 atoms icosahedron (all planes (111) like).

Some of these smallest particles with unusual structure have been already seen by Electron Microsocpy or by EXAFS (28,29). The larger particles are probably all shaped into boddies reminding of a sphere - cubo-octahedrons.

Needless to say that further analysis by EM and HREM of problems like the shape of smallest particles itself, the relation shape - epitaxy, shape - glueing layer between metals and carriers (oxide, hydroxide, silicate layers, etc.) and similar ones, is still highly desirable.

It is interesting to notice once more that there are already data available showing that the geometry of the smallest particles follows indeed, the indicated rules (27-29).

Particles smaller than a certain limit (arbitrary put e.g. at 4.0 nm) expose the low coordination sites in excessive amounts such that their - possibly- different catalytic behaviour should be observable (see table 1, ref.30).

table 1

Small particles of some transition metals adsorb hydrogen to a higher ratio: H_{tot}/M_{metal} than unity, as shown by KIp et al. (31). It means that the "valency" of some surface atoms of small metal particles of metals as Rh or Ir is different from that of atoms constituting macroscopic flat planes. This is a very interesting finding but unfortunately it also casts some doubts on determination of the total metal surface area (and from that, by using models - the particle size-) determination with supported metals (26). This discovery (21) demonstrates clearly how important it is to determine the particle size by other than adsorption methods, e.g. Electron Microscopy or by EXAFS.

Low coordinated sites

Discussion on the role of low coordinated sites and on electronic structure effects induced by diminishing the particle size (this affects also atoms on the planes) has not started yesterday.

Already in the fifties, vivid discussions took place between the school of Roginskij (32) and Kobozev (33) on one side and the school of Boreskov (34) on the other side; while the first mentioned scientists claimed a decisive role of the special (low coordinated) sites in all catalytic reactions, Boreskov stated that the steady state activity of metals in any reaction is a function of the electronic structure of metal atoms and varies with the metal particle size only marginally (within one order of magnitude in rates). An important progress in these matters has been achieved by Boudart (26,35), who recognized that there are two types of reactions.

I. structure insensitive, or better to say now - particle size insensitive and -

II. particle size sensitive reactions.

Simple hydrogenation reactions are an example of the first group, hydrocarbon reactions or ammonia synthesis (here the dissociative adsorption of N_2 is the sensitive step) of the second one (36).

It has been shown that the smallest metal particles have an energy spectrum which is rather different from the energy spectrum of bulk metals (37-39).

What is not known with a desired certainity is, whether this is also reflected by a substantial different catalytic behaviour of a metal atom in small and large particle surfaces.

There has been many speculations in the literature about the possible effects of the so called "electron defficiency" of small particles. It is in principle possible (although not yet proven) that when a metal particle is placed above, an electron acceptor center such as Al in SiO_2 structure, an electron is transferred from a metal particle to the support, making the particle positively charged. However, some people go so far that they expect a "catalytic transmutation (according to them) by electron transfer. A particle of Pd should behave more like Rh, that of Pt more like Ir, Au should become active as Pt, etc. (40-41). This matter has been discussed elsewhere (42,43) and thus only very briefly: a charge in a metal particle is very limited, it is localized and screened and it should not substantially influence the reactivity of all other metal surface atoms. The catalytic "alchymie" is not possible.

Side effects of the particle size variations

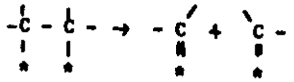
Small metal particles behave in many reactions differently from the large ones, but it does not always mean a size sensitivity of the main reaction. This has been correctly recognized already by Katzer (44), who also supplied the first examples showing that differences in the behaviour towards side reactions simulate a particle size sensitivity of a catalytic reaction followed (in his case - oxidation of ammonia and/or ethylene).

Lankhorst et al. (45) showed, that the skeletal reactions of hexane (see scheme 3 above) are characterized by an activity and a selectivity which does not vary too much in the critical range of particle sizes (1.8 - 7.0 nm), when the particles are kept clean. However, when the catalysts with different particle sizes were subjected to selfpoisoning (deposition of carbonaceous non-reactive layers formed from hexane), the activity (remaining activity) of small particles was much higher than that of the large ones. Also selectivity changes can be induced by that. Obviously, it is the behaviour towards a side reaction which induces a particle size sensitivity of the catalysts in hexane skeletal reactions.

Since the role of side reactions (in the last mentioned case - the selfpoisoning by carbonaceous layers) varies in its importance with various metals, and it can combine with the properties of a metal - one can expect all types of correlations of the catalytic activity with the particle size sympathetic or antipatic ones or functions with a maximum (16). When going from one metal to another, or from one reaction to another it is the task of science to establish, which is the intrinsic (not induced by side efefcts) correlation with a given reaction.

Multiple bond formation

Reactions of hydrocarbons are initiated usually by a dissociation of the first C - H bond. However, when thereafter a C - C bond has to be split, probably (at least) two H atoms have to be removed, to enable the splitting to run with a low activation energy:


(4)

There are good reasons to believe that also isomerization and dehydrocyclization can profit from the external multiple bond (external formation means "outside the molecule") formation, although in the latter cases, the internal multiple bond formation might be of greater importance (16, 46).

IN any case hydrogenolytic cracking is most likely most dependent of all on the formation of the metal carbon multiple bonds. In compliance with this expectation Kemball (47) and Van Broekhoven (48) established a very clear correlation between the propensity of metals to form the multiple bonds (a) and the reactivity of metals in cracking (b)

(a) Ru < Ni < Co < Ir < Rh << Pt < Pd

(b) Ru ≈ Ni ≈ Co < Ir < Rh ≤ Pt, Pd

Let us mention that the propensity of a metal to form metal-carbon multiple bonds can be, for example, determined by monitoring an exchange reaction of a hydrocarbon (CH_4 and cyclopentane have already been used to this end (48)) with deuterium.

Van Broekhoven decided to check whether the formation of multiple bonds is particle size sensitive. He used methane/D_2 exchange with which the ratio of CD_4/CH_3D in the initial product distribution can be taken as a measure of the multiple bond formation. The results are
fig.5 shown in figure 5 (49).

It is evident that small particles of various metals form multiple bonds less readily, than the large ones.

In compliance with the low activity in cracking the small particles form less readily carbonaceous layers and the curved surface is more difficult to be covered by carbonaceous layers than the flat planes. This explains the finding by Lankhorst et al. (45).

Let us mention in passing that the smallest particles of various metals have been prepared by filling the cages of zeolites by metal precursor solution, drying (oxidation of ligands) and reduction.
fig.6 An EM photo of such materials is shown in figure 6.

CONCLUSIONS

Practically used catalysts consist often of small particles. It is important to study the structure, shape, thermal behaviour, etc. of these particles. Surface structure, the local site geometriecs, are important for catalysis, as demonstrated by several examples above. In the mentioned studies the EM and EXAFS are very important tools.

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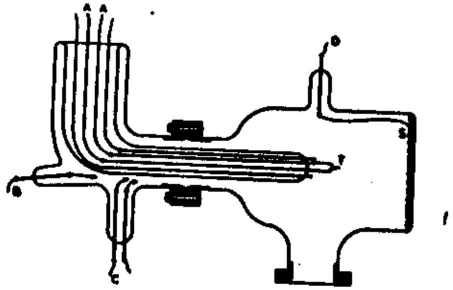
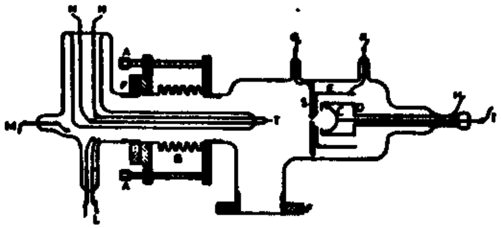
TEXT FOR THE FIGURES

1. Field emission tube
Field emission tube with a "probe-hole" facility
T - tip; S - screen; C - collector of electrons
(from ref.2, with permission)
2. F.E.M. picture of an Rh tip; various regions indexed
(from ref.4, with permission)
3. Heptane conversion on various single crystal planes.
Activity expressed as initial rate at 573K.
(from ref.12, with permission)
4. CO adsorbed on Pd(111). Various coordinations of CO indicated, occurring at various surface coverages (see the text)
(from ref.24, with permission)
5. Propensity of metals (here characterized by the CD_4/CDH_3 ratio measured at standard conditions) to form metal-to-carbon multiple bonds - as a function of the particle size. Pt, Ir and Ni.
(from ref.49, with permission)
6. Pt in zeolites; HREM by H.W.Zandbergen, Leiden University, 1987
The regular zeolite lattice has been partially removed by electron bombardement, in order to visualize better the Pt particles.



FIELD EMISSION TUBE



FIELD EMISSION PROBE-HOLE TUBE

figure 1

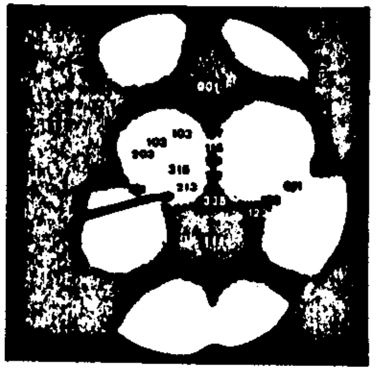


figure 2

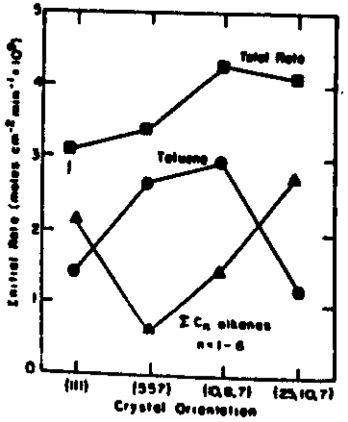


figure 3

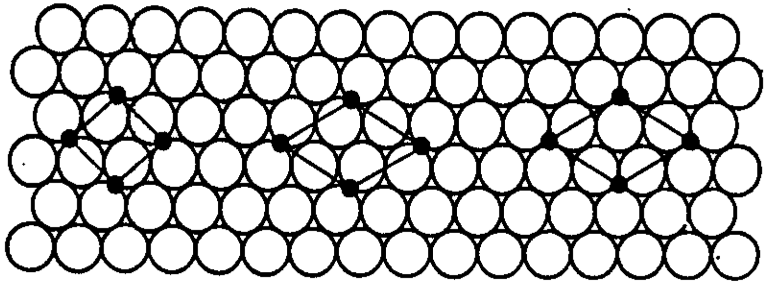


figure 4

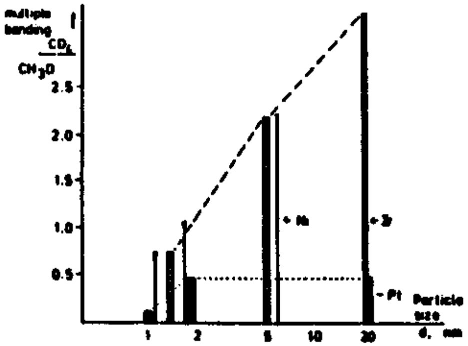


figure 5

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fig. 6

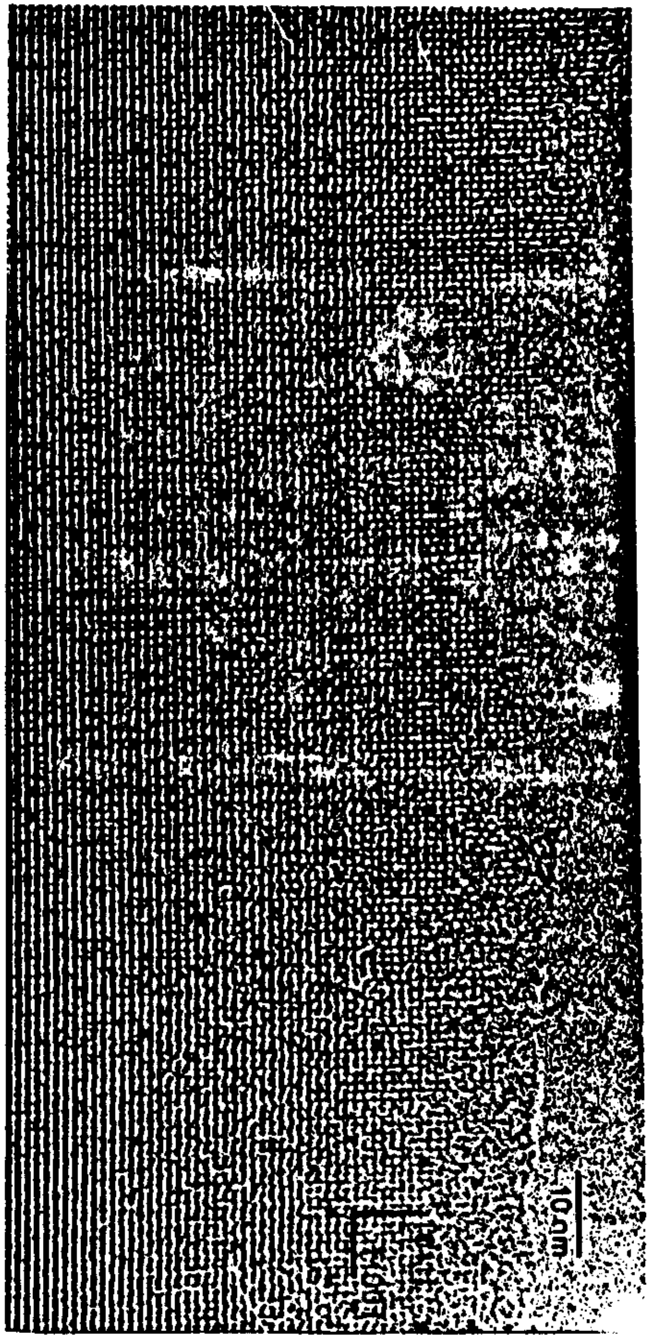

TABLE I

Size and surface properties of stable platinum crystals

Edge length		Total number of atoms in crystal	Fraction of atoms on surface	Relative number of diatoms in different states on surface			Average coordination number of atoms on the surface
In number of atoms	in Å			in vertices	on edges	on facets	
2	5.5	6	1	1	0	0	4
3	8.25	19	0.95	0.33	0.67	0	6.0
4	11	44	0.87	0.16	0.63	0.21	6.94
5	13.75	85	0.78	0.09	0.55	0.36	7.46
6	16.50	146	0.7	0.06	0.47	0.47	7.76
7	19.25	231	0.63	0.04	0.41	0.55	7.97
10	27.5	670	0.49	0.02	0.29	0.69	8.31
15	41.25	2 255	0.35	0.01	0.20	0.79	8.56
18	49.5	3 894	0.3	0.005	0.17	0.83	8.64
30	82.5	18 010	0.19	0.002	0.10	0.90	8.78
50	137.5	36 484	0.13	0.0006	0.06	0.94	8.87
∞	∞	∞	0	0	0	1	9

N.B. Calculations made for octahedral crystals. More exact calculations involving "unfinished" crystals, cubo-octahedrons, etc. do not differ appreciably.