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Problems in the Study of Supported Metal Catalysts

A.A.Slinkin

Our current understanding of catalysis on supported metals is reviewed, and the three most important problems still outstanding in this area of catalysts are discussed: 1) the sintering mechanism of the supported metals, 2) the structure and catalytic properties of small metallic crystals, and 3) catalysis by metal clusters. 96 references.

CONTENTS

I. Introduction 404
II. Sintering mechanism of supported metal catalysts 404
III. Structure and catalytic properties of small metallic crystals 406
IV. Catalysis by metal clusters 409

I. INTRODUCTION

Among the various problems encountered in the study of the structure and catalytic properties of supported metals the following appear to be the most important:

1) the sintering mechanism of supported metal catalysts

2) the structure of small metal crystals, and their catalytic properties

3) catalysis by metal clusters.

Without attempting a comprehensive treatment of these complex problems, we shall formulate the basic concepts and approaches which have been developed for their solution.

II. SINTERING MECHANISM OF SUPPORTED METAL CATALYSTS

The scope of theoretical and experimental studies of the sintering of supported metal catalysts has increased in recent years because of the great practical importance of this problem in the development of stable catalysts, and also because many of the theoretical problems to be solved are relevant to catalysis as a whole, i.e.: 1) the interaction and diffusion of metal atoms on the metal surface, 2) the interaction of metal microcrystals and atoms with the carrier, 3) the effect of various gases on the sintering process, 4) the effect of impurities in the metal and in the carrier on the sintering mechanism.

We shall briefly review the basic theoretical considerations and some of the most important experimental results in this field of research.

1. Model of Particle Growth Through the Migration, Collision, and Coalescence of Crystals

A phenomenological description of these processes was recently developed by Ruckenstein and Pulvermacher[1,2] (the RP model) and analysed by Wynblatt and Ahn[3]. Sintering is described in terms of binary collisions on a plane surface, and rate limitation is associated either with the migration or with the coalescence of the particles. In either case we can write

$$\left[\frac{S_0}{S}\right]^n = 1 + (\text{const})\,t \qquad (1)$$

or

$$\frac{dS}{dt} = -kS^n, \quad n = 3+m,$$

where n and m are integers, and m is related to the diffusion coefficient (D) and to the radius of the particle (R) by the expression

$$D = c(1/R)^m;$$

S_0 is the initial value of S (the aggregate surface area of particles per unit area of carrier surface).

This model can be used to calculate the distribution of particles for either migration or coalescence as the rate-limiting step of the growth process. However for $n = 3$ the model predicts a diffusion coefficient independent of particle size, which is difficult to accept. The formalism of the RP model was extended by Wynblatt and Jostein[3], who calculated the coalescence times (τ_c) and the migration times (τ_p) of the particles on the surface (see Table).

Calculated coalescence and migration times of particles on the surface*.

$2R$, Å	τ_c, s	D_p, $cm^2 s^{-1}$	τ_p, s
25	$3.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-18}$	12
100	$8.9 \cdot 10^{-2}$	$5.0 \cdot 10^{-16}$	$3 \cdot 10^4$
250	3,5	$1.3 \cdot 10^{-17}$	$1.2 \cdot 10^7$
2500	$3.5 \cdot 10^4$	$1.3 \cdot 10^{-21}$	$1.2 \cdot 10^{13}$

* $T = 700$ °C; the migration path is $10 \times 2R$.

The coalescence time is seen to be much shorter than the time for migration of the particle over a significant distance, and therefore the rate-limiting step of the sintering process is migration rather than coalescence. From the tabulated results and their associated calculations we conclude that the growth of particles can be limited by migration only for particle sizes below 50 Å. The RP model has been criticised[4,5] on the following grounds:

1) it ignores the energetic and morphological non-uniformity of the surface;

2) it fails to explain the observed increase in the dispersion of the metal at high temperatures in an O_2 atmosphere;

3) there is no independent demonstration that the motion of the particles is sufficient to account for sintering.

2. Model of Particle Growth Through the Migration of Atoms or of Sub-atomic Molecular Units

This model, which was developed by various workers[6-8], is illustrated in Fig. 1. Particles grow as a result of matter transport by two mechanisms: diffusion through the gas phase and diffusion on the carrier surface.

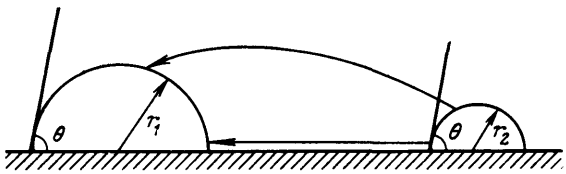


Figure 1. Transfer of matter between two particles on a plane surface[6].

The angle θ is given by the formula

$$\gamma_s = \gamma_{ms} + \gamma_m \cos\theta,$$

where γ_S and γ_m are the surface tensions of the carrier and of the particle respectively, and γ_{mS} is the interfacial tension. The chemical potential μ of the particle depends on the particle radius r according to the Gibbs–Thomson equation

$$\mu = \mu_0 + 2\gamma_m \Omega / r,$$

where Ω is the atomic volume.

Thus large particles will grow at the expense of the smaller particles, whose chemical potential is greater, leading to an overall decrease in the surface energy of the system. According to this model the atomic mechanism of the sintering process may involve three steps[7]: 1) removal of a metal atom (or molecular unit) from the crystal, and transfer to the carrier; 2) migration of the atomic (or molecular) particle on the carrier surface; 3) capture of the migrating atoms (or molecules) by the crystals during collisions.

In this model the sintering process can be described with allowance for specific physicochemical features of the system. For example, in a supported Pt system the diffusing species are Pt atoms in a reducing medium and PtO_2 or PtO particles in an oxidising medium. The rate of growth of the particles is small in a reducing atmosphere because the sublimation energy (which appears in the exponential term of the rate constant) is 135 kcal mole^{-1} for Pt. On the other hand since the activation energy for the removal of a Pt atom as PtO_2 is only ~ 42 kcal mole^{-1} we expect the rate of growth to be substantially higher in an oxidising atmosphere.

This sintering mechanism predicts the following phenomena[3]:

1) the sintering rate should increase with the partial pressure of O_2;

2) stronger wetting of the carrier surface by the particles (or an increased interaction between the diffusing atom and the defects in the carrier) should lower the sintering rate, and in this way it should be possible to control the sintering process by adding impurities to the carrier or metal crystal surface;

3) the growth of particles in an O_2 atmosphere should be strongly dependent on the enthalpy of the reaction

$$M(s) + xO_2(g) = MO_{2x}(g).$$

On this basis we can define the following stability series for supported metals in an oxidising atmosphere: Os < Ru < Ir < Pt < Pd, Rh;

4) the stability under reducing conditions is determined by the heat of sublimation, leading to the following stability sequence: Pd < Rh, Pt < Ru < Ir < Os.

Neither of these theories can at present be accepted with full confidence, though a recent experimental paper[9] has confirmed the stability sequences predicted for Rh, Pt, and Ir supported on Al_2O_3. The problem is still being actively discussed[10,11], and a model of the sintering process allowing for the transfer of atoms has recently been proposed by Ruckenstein[8].

We shall now examine some examples of sintering phenomena which fall outside the scope of existing theories and need new conceptual approaches.

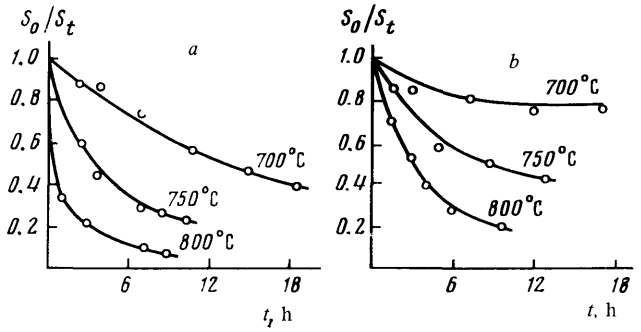


Figure 2. Sintering kinetics of $Pt-Al_2O_3$ catalysts: (*a*) in air and (*b*) in argon[12].

The sintering kinetics of a $Pt-\alpha-Al_2O_3$ (0.036 wt.% Pt) catalyst[12] in air and in argon are shown in Figs. 2*a* and 2*b*. The sintering rate is much greater in air than in argon: the exponent n in Eqn. (1) takes the value 2 and 3 respectively, in keeping with the RP theory. However the sintering rate in N_2 quite unexpectedly goes through a maximum. This is ascribed[12] to chemical interaction between N_2 and Al_2O_3 at high temperatures (800 °C), leading to changes in the morphology of the carrier and in the sintering mechanism.

Electron microscopic studies[13] have confirmed that sintering is much faster in an oxygen atmosphere than in a vacuum. However the most fundamental result of this work was the first experimental observation of the motion of Pt crystals on the surface of graphite. The authors were able to monitor the tracks of particles moving on the graphite surface during combustion of the graphite in oxygen. Very surprisingly, particles of diameter ~ 1000 Å were found to move: this is theoretically impossible, but it can happen in this case because of the large decrease in interfacial energy resulting from the presence of O_2.

O_2 interactions on supported Pt crystals can lead to another effect not predicted by theory: dispersion of the crystals[14,15]. Pt crystals supported on Al_2O_3 whose diameter in air was initially 31 Å were found[14] to increase in size to 107 Å after a sintering treatment in air followed by slow cooling. However when the sample was re-heated in air to 500 °C and slowly cooled to 20 °C dispersion of the crystals was observed (to a diameter of 41 Å). This effect can be explained through the

formation of Pt(IV)–Al_2O_3 complexes, with a critical formation temperature of ~500 °C. This reaction at the interface between the metal and the carrier is accompanied by a large increase in the stresses applied to the metal, and these stresses are relieved by the cleaving of the crystals.

A different explanation of the same effect is given in Ref.15. It is pointed out that the PtO_2 molecules breaking away from the microcrystals can be stabilised on non-uniformities of the carrier surface and act as nuclei for new crystallites. Allowance for the inhomogeneity of the carrier surface is a significant refinement of the theoretical model, which is usually confined to a homogeneous surface. For example, the concept[16] of "trapping centres" from which microcrystallites can be released only by the expenditure of activation energy has been confirmed[17] by a demonstration that the disperseness of Pt on graphitised carbon increases (from a particle diameter of 68 Å to 19 Å) as the extent of burn-off is increased from 0 to 50%. In this case the dispersion effect arises from an increase in the energy non-uniformity of the carrier rather than from an increase in its surface area.

It is important to note that the re-dispersion of large metal crystals has been observed not only in supported platinum catalysts but also in metal–zeolite systems, in which cations are formed in an oxidising atmosphere and diffuse into the bulk of the zeolite[18,19].

Some of the most interesting publications discuss the chemical nature and the mechanism of action of the "trapping centres" which inhibit the sintering process. Thus it has been shown[20] that Pt microcrystals deposited on γ-Al_2O_3 by evaporation and decomposition of tetra-ammine complexes can be sintered in a N_2 or O_2 atmosphere, whereas crystals prepared from H_2PtCl_6 are stable up to 800 °C. It is suggested that sintering is inhibited by Cl^- ions. A similar inhibition effect by Mo^{2+} ions (added to the carrier) on the sintering of Pt and Pd was reported by Ermakov and coworkers[21].

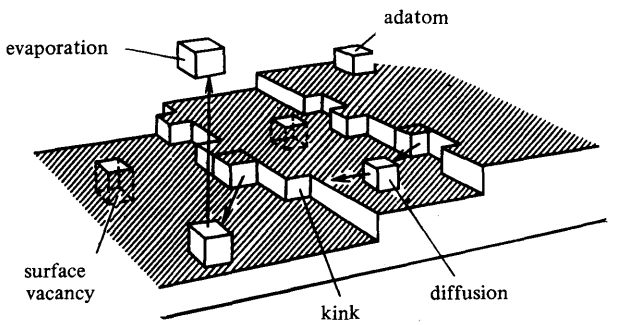


Figure 3. Elementary acts in diffusion on a crystal surface[24].

Takami and coworkers[22] made the important discovery that Rh–$MgWO_4$ catalysts have a high activity towards the reforming reaction of hydrocarbons with water vapour. Surprisingly, the surface area of the $MgWO_4$ sample was only 3–5 $m^2\ g^{-1}$, and most of the Rh was stabilised as large crystals. The high activity of these catalysts was explained by the formation of Rh^{3+} cations, which can replace Mg^{2+} in the tungstate lattice (isomorphous substitution). If tungstates of other metals (Be, Zn, Ca, Ba) are used as carriers the activity drops by a factor of 5–15. The possibility of dissolving atoms (or cations) of the metal in the lattice of the carrier was recently demonstrated (for Au atoms in MgO or Al_2O_3 lattices) by analysing the fine structure of the X-ray absorption spectra[23]. This possibility must be borne in mind when the structure and catalytic properties of supported catalysts are discussed.

The sintering processes discussed so far lead to a change in size of the metal crystals, and to a corresponding change in catalytic activity. However diffusion processes can occur not only between crystallites but also on the surface of a given crystallite[24]. The elementary steps in the diffusion of atoms on a crystal surface are shown in Fig.3. Evidently, the "healing" of vacancies and the disappearance of kinks and steps can lower the activity without altering the size of the crystal. This process, termed "qualitative sintering", has been observed in Pd–Al_2O_3.SiO_2 catalysts[25], in which sintering is inhibited by the addition of Al^{3+}, La^{3+}, and Th^{4+} cations. The stabilisation mechanism associated with the presence of these cations is not fully understood, but one possible explanation is that the cations prevent "internal" sintering† by being adsorbed on defects contributed by surface centres.

III. STRUCTURE AND CATALYTIC PROPERTIES OF SMALL METALLIC CRYSTALS

For the last 20 years the key problem in the study of catalysis by supported metals has been to characterise the catalytic and structural properties of small metal crystals, and in more recent years this problem has attracted a great deal of attention[26–30]. We shall dwell on some aspects of this problem, i.e.: a) the structure of the crystals, and their catalytic and adsorption properties; b) interactions between the reaction system and the supported catalyst; c) the formation and properties of surface structures.

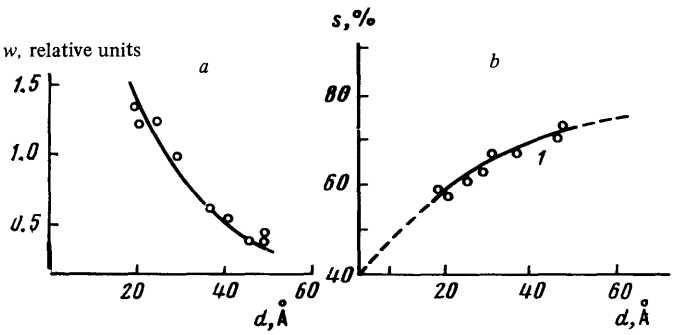


Figure 4. (*a*) velocity *w* and (*b*) selectivity *s* of the dehydrogenation of 2,3-dimethylbutane against disperseness of the Pt in a Pt–carbon catalyst[31] (curve *1*).

The number of publications on the effect of crystal size on catalytic activity and selectivity has continued to grow. It was shown[31] that the overall rate of dehydrogenation of 2,3-dimethylbutane by Pt–carbon catalysts decreases as the

† A process by which defects can be removed from the surface of microcrystals without sintering of the crystals.

average size of the Pt crystals increases, but the selectivity of the formation of 2,3-dimethylbut-1-ene increases (Fig. 4). This is ascribed to differences in the structure of intermediate complexes adsorbed on small and on large crystals, and is quoted as an example of a hindered reaction. Whether a reaction is hindered or unhindered is largely determined by the range of crystal size. The hydrogenation of benzene on $Pt-Al_2O_3$ is unhindered in the 10–50 Å crystal size range[32], whereas on Ni crystals ~5 Å in size the same reaction appears to be hindered[33]. A similar situation was observed in a study of the hydrogenolysis of ethane[34]: the specific activity was independent of the dispersion of the Ni catalyst in the range 15–70 Å, but it increased by a factor of 3 for a crystal size of ≤10 Å. The rate of oxidation of CO was found[12] to be extremely sensitive to the crystal size of the Pt catalyst.

This behaviour has been discussed both in terms of the structural features of small crystallites and by allowing for possible changes in electronic properties of the crystals (though these characteristics are often interrelated). For example, the decrease in specific activity of Ag crystals of increasing size, and the increase in their selectivity towards the formation of ethylene oxide or of CO_2 in the oxidation of ethylene, have been explained[35] by postulating two types of centre, corresponding to two forms of chemisorbed oxygen. Atomic oxygen, localised on atoms, occurs at the corners, edges, and growth steps of microcrystals: this form is very active, and leads to the formation of CO_2. Molecular oxygen, adsorbed on crystal faces, oxidises ethylene to ethylene oxide[35]. The 40-fold change in activity of Pt crystals towards the D_2 exchange with CH_4 on increasing the particle size from 9 to 100 Å is ascribed[36] to an increased proportion of the thermodynamically more stable (111) faces, which are not effective in catalysis. Thus the catalytic activity and selectivity of randomly oriented supported Ni crystals was found to be different from that of similar crystals in which the (111) and (110) faces were preferentially developed[37,38]. The oriented Ni crystals are more active towards the hydrogenation of ethylene, and they give a higher yield in the hydrogenolysis of n-heptane.

The concept of hindered and unhindered reactions is further developed in a study[39] of the isomerisation mechanism of 2-methylpentane and n-hexane on supported Pt crystals of different disperseness, allowing for the enhanced activity of atoms on corners or edges. The reaction mechanism (Fig. 5) includes the following steps:

1) weak adsorption on a Pt atom, localised on a crystal face (c_f);
2) surface diffusion to a reaction centre (edge atom, c_e);
3) formation of strongly dehydrogenated fragments on this centre;
4) rearrangement of the strongly adsorbed particles;
5) re-hydrogenation, surface diffusion, and desorption of the weakly adsorbed isomerised molecules.

A new classification of catalytic reactions has been proposed[39]. In reactions of type I all the surface atoms of the catalyst are equally active, and neither the rate nor the selectivity depends on the disperseness of the particles. In reactions of type II the number of reaction centres is greater than the number of weakly adsorbed molecules, and in this case the selectivity only is a function of disperseness. If the number of reaction centres is smaller than the number of weakly adsorbed molecules (type III) or if surface diffusion is very slow (type IV) both the selectivity and the specific reaction rate become a function of crystallite size.

Many workers have reported large differences in the adsorption and catalytic properties of metal atoms having different coordination. Thus it has been shown[40] that the n-heptane reforming reaction on supported rhodium catalysts involves atoms located on crystal faces, whereas the aromatisation reaction is due to edge atoms of Rh. Three types of centre have been defined[41] on a stepped metal surface: *A* centres (localised within a plane face), *B* centres (edge atoms), and *C* centres (corner atoms or atoms localised above the surface of a plane face). Each of these types of centre is thought to be responsible for a specific reaction involving olefins (*cis–trans*-isomerisation, migration of the double bond, hydrogenation). A similar explanation has been given[42] for the dependence of the rate of hydrogenation of cyclopropane, methylcyclopropane, and propylene on the disperseness of the Pt.

Calculations of the numbers of edge and corner Ni atoms in defect microcrystals have been used[43] to relate the amount of irreversible H_2 chemisorption to the disperseness of the Ni crystals.

Changes in catalytic activity and selectivity resulting from changes in crystal size may be due not only to structural differences between large and small crystals but also to a size dependence of the electronic properties of crystals. For example, the structure of the valence band of small crystals may be different from that of large crystals, since in small crystals: a) the potential may differ from the periodic lattice potential as a result of the presence of free valence electrons, b) the density of surface states may be greater than the density of electronic states, and c) the electronic state density may be affected by the presence of the carrier.

Thus in Pt crystals of 12–20 Å size supported on SiO_2 the edge of the valence band is shifted downwards by 1.5 eV relative to the Fermi level, and the valence band structure is quite different from that of a massive Pt crystal. On the other hand the electronic properties of Pt crystals 20 Å or more in diameter are identical to those of massive Pt.[44]

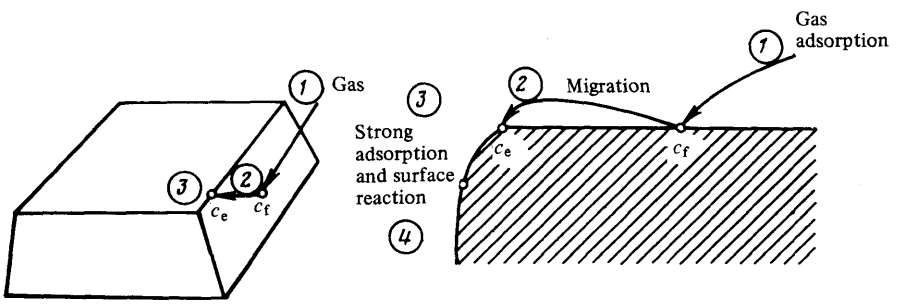


Figure 5. Mechanism of the isomerisation of 2-methylpentane and n-hexane[39].

Changes in crystal size have been shown[45] to influence the ratio of the ionisation potential to the electron affinity, and also the properties of the orbitals. Furthermore, the nature of the chemisorption bond may vary quite substantially under the influence of the carrier (and therefore as a function of the size of the crystals).[46] It is difficult at present to compare these theoretical calculations with experiment, but some workers have used calculated results to explain experimental findings. Thus the specific activity of Pt towards the methanation of CO increases by two orders of magnitude when the disperseness of the metal is increased 200-fold, an effect explained by the formation of the more weakly adsorbed, linear form of CO on the smaller crystals. On Pd, on the other hand, the activity is unaffected by the particle size of the metal though it is strongly dependent on the nature of the carrier (Al_2O_3, SiO_2), and this is ascribed to electronic interactions between the carrier and the metal microcrystals[47].

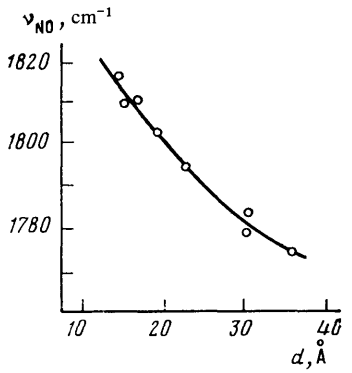


Figure 6. ν_{NO} against disperseness of the Pt.[48]

Changes in the nature of the chemisorption bond as a function of the disperseness of the metal must be allowed for when discussing catalytic systems, since this effect can influence both the rate and the selectivity of the process. As shown in Fig. 6, the frequency of stretching vibrations of NO irreversibly adsorbed on Pt crystals decreases as the crystal size increases, i.e. the energy of the N–O bond decreases[48]. The hydrogen bond strength and its charge also depend on the size of the Ni crystals[49]: these parameters can determine the reactivity of the adsorbed hydrogen. It has been shown that one form of ethylene adsorbed on Pd can be hydrated only by the negatively charged form of hydrogen, the positively charged form being completely inactive[50].

In this discussion of the structure and catalytic properties of supported metal microcrystals we have so far ignored changes induced by the reacting system. Yet very substantial effects of this type are possible: a) dispersion, or sintering, of the crystals, b) the development of facets which are more stable under the conditions of the catalytic reaction, c) internal reconstruction of the microcrystals without change in crystal size, and d) the formation of new phases on the catalyst surface.

Dispersion and sintering of supported metal crystals during a catalytic reaction are well known effects. Recently published data indicate a surprisingly fast reorganisation of a Ni surface under the influence of H_2 under conditions of hydrocarbon reforming with water vapour (due, no doubt, to the formation of different nickel hydrides[51,52]). It is interesting to note that the sintering of Ni in H_2 is much faster than the sintering of Pd.

A rearrangement of the surface facets of Pt [e.g. from (111) to (100)] under the influence of sulphur, leading to a decrease in surface free energy and in catalytic activity, has been demonstrated[53,54]. This effect may occur on other metals also.

The internal rearrangement of the microcrystals under the influence of the reacting species is particularly interesting. The main contribution to this work came from Boudart and coworkers[55–59], and it concerns the variations in the rate of the NH_3 synthesis on Fe crystals 15–300 Å in diameter stabilised on an MgO surface. The reaction rate increases as the particle size increases, but it also increases (for a constant crystal size of 15 or 40 Å) if the crystals are pre-treated in a mixture containing nitrogen. This pre-treatment causes a surface rearrangement (without changing the particle size) accompanied by a decrease in surface magnetic anisotropy and hence in the adsorption of CO. The underlying cause of these effects is shown to be the formation of C_7 centres#, which are active towards the NH_3 synthesis reaction.

The formation of a new phase on a catalyst surface during the reaction, and the structure of this phase, can influence the course of the reaction to a very large extent. This is clearly shown by studies of single-crystal faces[60,61]. For example, a disordered layer of carbonaceous products, which does not inhibit the reaction, is formed on the surface of stepped platinum faces during the hydrogenolysis of n-heptane. However the dehydrocyclisation reaction (with formation of toluene) occurs only on stepped crystal faces covered with an ordered carbon layer, and this layer is not formed on perfect (111) faces.

In addition to the oriented or non-oriented carbon structures formed by interactions with hydrocarbons on metal surfaces we can expect oxide, nitride, sulphide, and other structures to result from interactions with other compounds. A detailed analysis of the properties of these surface phases can be relevant to the identification of the mechanism of adsorption and catalytic processes. Experimental and theoretical studies of the interaction of oxygen with metal surfaces have been actively pursued in recent years[62–66]. By using monocrystal surfaces it has been possible to identify the various steps of surface and bulk reactions leading to the formation of two-dimensional and three-dimensional phases and to surface reconstruction.

Important results were obtained in studies of metal–oxygen structures formed by the action of O_2 on metal microcrystals. Fully disordered surface layers on Pt microcrystals following O_2 adsorption were observed[67] by the electron density radial distribution method. It was shown[68] that the deactivation of supported Pt microcrystals during the low-temperature oxidation of NH_3 is not due to a sintering process, but to the formation of an oxide layer several atoms thick or even to full oxidation of small crystals. These results force us to revise our views on the stability of the precious metals towards oxidation. Interactions with O_2 (under certain conditions) on Ni microcrystals stabilised by a carrier lead to the formation of surface nickel–oxygen structures of a quasi-metallic nature in which the oxygen shows a number of interesting properties[69], e.g.:

a) it acts as an additional centre for H_2 chemisorption, leading to a substantial increase in H_2 adsorption as compared with a clean Ni surface (Fig. 7);

b) it readily diffuses into the bulk of the crystal;

A surface centre with seven nearest-neighbour iron atoms.

c) the nickel–oxygen structure (unlike to NiO phase) is easily reduced by hydrogen.

We should note that the polarisation of the nickel atom is quite different in the nickel–oxygen structure and in NiO microcrystals, as shown by the large difference in adsorption capacity for ethylene (Fig. 8). This result suggests that the interaction of ethylene with the Ni^{2+} cation is much stronger than the interaction with the polarised nickel atom in the nickel–oxygen structure[70].

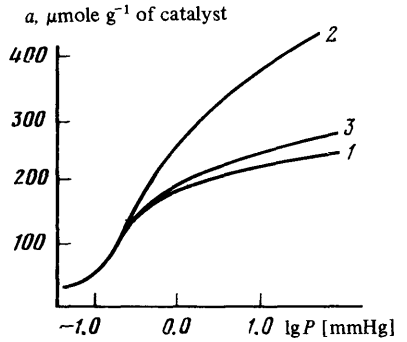


Figure 7. Adsorption of H_2 at 22 °C on supported Ni microcrystals[69]: *1*) clean surface, *2*) and *3*) surface covered with oxygen added at 150 and 300 °C respectively.

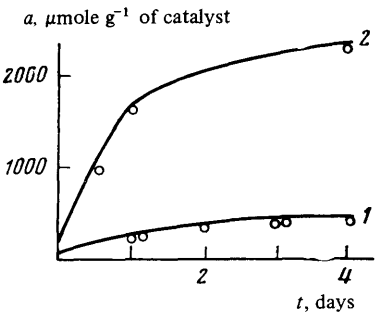


Figure 8. Kinetics of the adsorption of C_2H_4 at 22 °C: *1*) clean surface of supported Ni microcrystals and nickel–oxygen structure, *2*) supported NiO microcrystals[70].

IV. CATALYSIS BY METAL CLUSTERS

We shall now briefly consider the problems which arise in studies of catalysis by metal clusters (mainly, bimetallic clusters). These problems are attracting a great deal of attention because of their great theoretical and practical importance, and many recent results have already been critically reviewed[71–75].

There are several reasons for the current interest in this work: a) the prospects of a theoretical analysis of the interactions between atoms in a cluster and between the cluster and the carrier[76,77]; b) the large difference in selectivity between the bimetallic clusters and the component metals; c) the large difference in catalytic activity between the clusters and the component metals.

Theoretical analyses of the physical, adsorption, and catalytic properties of bimetallic clusters usually take account of two effects resulting from the addition of one metallic component to another:

1) the geometric factor (or "ensemble" effect),
2) the electronic factor (or ligand effect).

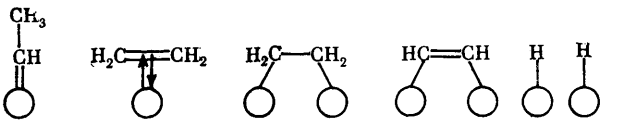


Figure 9. Adsorption forms of C_2H_4 on clusters of one, two, and four atoms respectively.

The geometric factor is clearly illustrated in Fig. 9, which shows various forms of ethylene adsorbed on nickel, requiring the presence of one-, two-, and four-atom ensembles on the surface respectively. Evidently, an increase in the amount of the second component (e.g. copper) on the surface lowers the probability of forming multi-atomic ensembles.

The electronic factor is far more complex. The "rigid band" model has long been used to discuss the physical and catalytic properties of alloys, and supported bimetallic clusters can be treated as a special case of alloy catalysts. Essentially the model states that an atom (for example, nickel) when introduced into the lattice of another component (for example, copper) loses its individuality, and its electronic levels are incorporated in the common *d*-band of the alloy. This model successfully describes the magnetic properties of alloys at relatively low concentrations of the additive, when the alloy remains ferromagnetic[78]. However there is evidence (experimental as well as theoretical) that the foreign atom can retain its individuality to a large extent[79,80].

The X-ray photo-emission spectra of the valence band of Ni–Cu alloys[81] are shown in Fig. 10. We note that the width and the shape of the Ni *d*-band are substantially unaffected by the addition of Cu. Characteristically, this *d*-band intersects the Fermi level at all compositions: the Ni atoms always have free *d*-levels and the electronic interaction with the Cu atoms is not very marked. This conclusion is confirmed by the failure to observe a shift in the frequency of the C–O bond vibration in the i.r. spectra of CO adsorbed on Ni–Cu alloys of increasing Cu content[82]: the only change was a decrease in the intensity of the band associated with the bridge form of CO adsorption. This decrease was ascribed to the geometric factor, i.e. to the decrease in the number of doublet centres on the alloy surface as the alloy is progressively diluted with copper.

However the existence of electronic interactions between the Ni and Cu atoms in this system has also been demonstrated[83]. As the alloy is made richer in copper both the intensity of the vibrations of the bridge form of adsorbed CO and the frequency of the vibrations of the CO bond in the

linear (*A*-band) as well as in the bridge (*B*-band) form decrease (Fig. 11), indicating an increase in the electron density on the nickel atoms. Magnetic data (Fig. 12) also show that an increase in the Cu content of the alloy is accompanied by a decrease in the number of bonds to the metal surface from 1.8 (for Ni) to 1.0 (for Cu), i.e. by a transition from the bridge to the linear adsorption form. It is interesting to note that Ni^{2+} ions in partially reduced Ni–SiO_2 catalysts lower the intensity of the band arising from the multi-centre form of CO adsorption, i.e. they act as diluents (like Cu atoms) by lowering the probability of finding clusters of several Ni atoms on the surface[84].

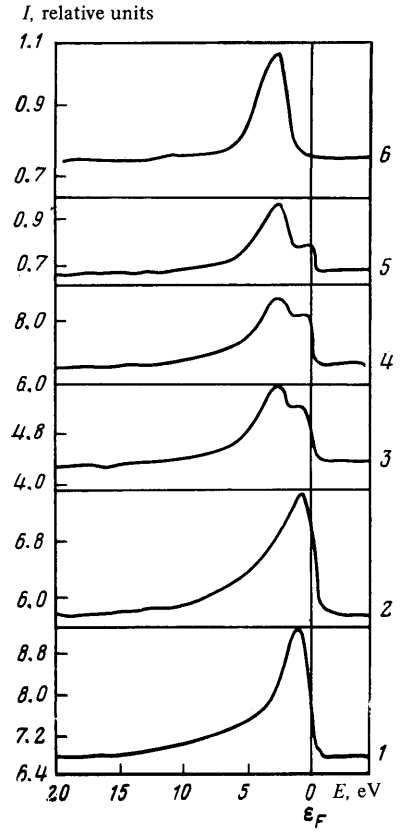


Figure 10. X-ray photo-emission spectra of the valence band of Ni–Cu alloys[81]: *1*) Ni, *2*) Cu(12%)–Ni(88%), *3*) Cu(44%)–Ni(56%), *4*) Cu(46%)–Ni(54%), *5*) Cu(74%)–Ni(26%), *6*) Cu.

In addition to demonstrating the presence of clusters in the Cu–Ni system recent work has shown that clusters can exist in other systems too. For example, Mössbauer spectral measurements have revealed the presence of Pd–Fe clusters in Pd and Fe supported on η-Al_2O_3.[85,86] The Mössbauer effect has proved very valuable in studies of electronic interactions in clusters. Thus iron in Pt–Fe clusters supported on γ-Al_2O_3 proved to be inactive (as compared to pure iron) towards the synthesis of hydrocarbons from CO and H_2.[87]

This effect may be related to the observed decrease in electron density on an Fe atom in a cluster due to interaction with the more electronegative Pt atom.

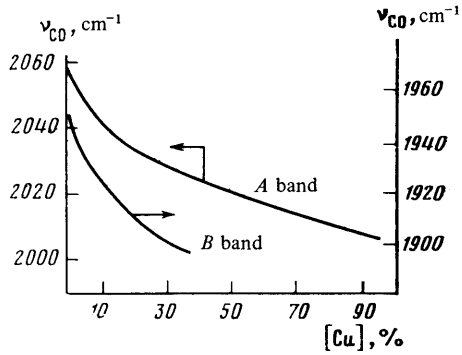


Figure 11. Variation of ν_{CO} for the *A* and *B* bands against Cu content of Ni–Cu alloys[83].

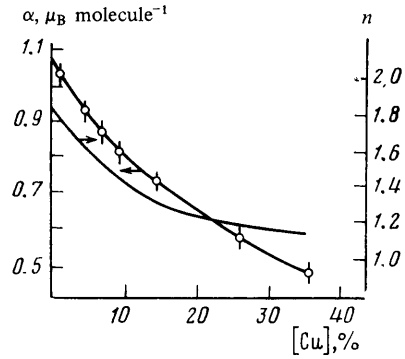


Figure 12. Effect of Cu concentration in a Ni–Cu alloy on the magnetisation (α) and number of bonds (n) per molecule of CO.[83]

Large electronic effects have been observed in clusters based on Pt and Sn as a result of electron transfer from Sn to Pt.[88] For example in the series Pt < Pt_3Sn < PtSn < $PtSn_2$ the surface is progressively enriched in Sn atoms, with a corresponding decrease in the strength of the bond between the surface and adsorbed CO, C_2H_4, and D_2 molecules. The downward shift of the ethylene desorption temperature on going from Pt_3Sn to PtSn is shown in Fig. 13. Typically, whereas the adsorption of ethylene on pure Pt is accompanied by a significant amount of self-hydrogenation the addition of Sn causes the adsorption of ethylene to be reversible. This is ascribed to the absence of Pt atomic ensembles on the surface of PtSn, but the effect could equally well be explained by an increase in electron density on the Pt atoms. Surprisingly, adsorbed CO molecules appear to "draw out" the Pt atoms from layers immediately below the surface and thus enrich the surface with Pt, but this effect is reversible and the initial state of the surface can be restored by pumping out the CO at room temperature.

Similar phenomena have been observed in the adsorption of O_2 on a Ni–Au alloy[89]. The alloy surface, initially consisting mainly of gold atoms, is found to be enriched in nickel atoms after O_2 adsorption: this effect is explained by the preferential attraction of Ni atoms towards the surface, resulting from the fact that the O–Ni bond energy is greater than the energy of the O–Au bond. These effects cannot be ignored when discussing the adsorption and catalytic properties of supported Bi- and polymetallic clusters.

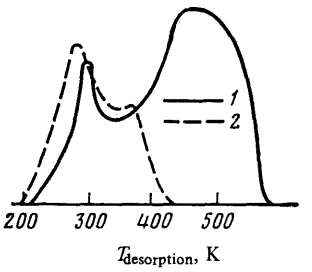


Figure 13. Desorption of ethylene from (*1*) Pt_3Sn and (*2*) PtSn surfaces.

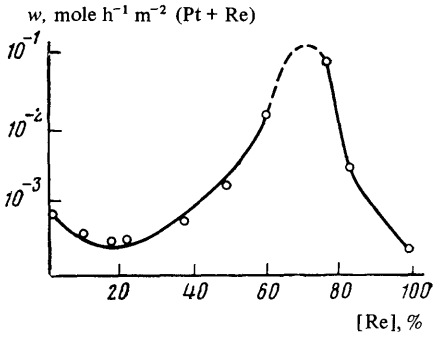


Figure 14. Specific catalytic activity *w* against concentration of Re in the hydrogenolysis of cyclopentane on $Pt–Re/Al_2O_3$ catalysts[93].

Thus in platinum–tin clusters the presence of the second component can have a powerful influence on the electronic state of the active centre[88], and hence on the type of interaction between the centre and adsorbed molecules. Similar effects were reported for additions of Sn to Pd or Ni supported on SiO_2.[90] The formation of carbonaceous deposits during the dehydrogenation of various compounds is suppressed if the Pd or Ni catalyst is alloyed with tin, suggesting a decrease in the energy of the bond between the reactants and the catalyst. According to measurements by X-ray photo-electron spectroscopy (XPES) the electronic structure of Pd and Ni is strongly affected by additions of Sn.

Another example of the decrease in bond energy between the reactant and the active centre is given in Ref. 91: the Pd–Au alloy (60 at.% Au) is approximately 50 times more active than Pd towards the oxidation of hydrogen by oxygen, showing that the energy of the bond between oxygen and a Pd atom is decreased by the presence of Au atoms on the surface.

Some of the most interesting Pt-containing clusters are the Pt–Re clusters supported on α- and γ-Al_2O_3. I.r. spectral data on CO adsorption have shown[92] that electron transfer from Re to Pt is responsible for the interactions in this alloy. The catalytic properties of this system towards the deuterium exchange and hydrogenation of benzene, the hydrogenolysis of cyclopentane and butane, and the dehydration of 1,1,3-trimethylcyclohexane suggest that in most cases the activity goes through a maximum (or several maxima): the maximum activity can be greater than the activity of the initial components, as shown by the change in specific activity as a function of composition of the cluster during the hydrogenolysis of cyclopentane (Fig. 14).[93] Within the framework of the "local" model these results can be explained[93] by the tendency of the cluster (depending on its composition) to acquire catalytic properties similar to those of Ir and Os as a result of electronic interactions between the components: these metals are known to be catalytically more active than Pt and Re towards the reactions under study.

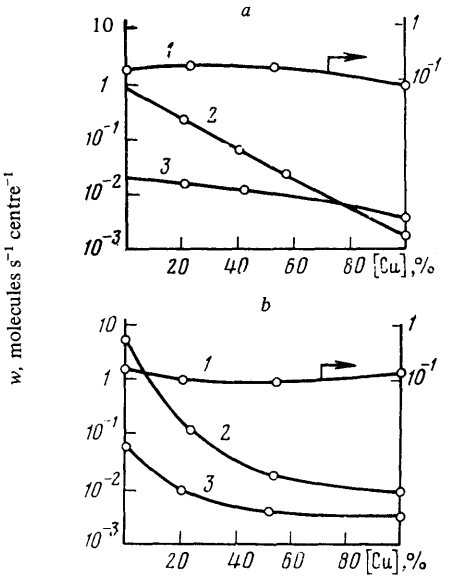


Figure 15. Specific catalytic activity *w* against composition of supported (on SiO_2) Cu–Ru (*a*) and Cu–Os (*b*) catalysts[94]: *1*) dehydrogenation of C_6H_{12}, *2*) hydrogenolysis of C_2H_6, *3*) hydrogenolysis of C_6H_{12}.

We shall close this review with a brief mention of the effect of composition on the selectivity and catalytic action of the cluster. This problem, as mentioned above, is currently one of the main areas of research on catalysis by clusters. The most important results obtained so far have already been critically reviewed[71–74]. Among the most interesting studies

in this area is Sinfelt's work[74] on the catalytic properties of Ni–Cu clusters towards the dehydrogenation of cyclohexane and the hydrogenolysis of ethane: a large increase in the amount of Cu in the alloy has practically no effect on the specific rate of dehydration of cyclohexane, whereas the rate of hydrogenolysis of ethane falls by about three orders of magnitude when as little as 5 at.% of Cu is added to the Ni. Similar results (Fig.15) were obtained for supported Ru–Cu and Os–Cu clusters in the same reactions[94]. Interactions in the Ru–Cu system have been studied by the XPES method[95]. It was shown that the Ru microcrystals are covered by Cu, and that heat treatment in H_2 produces a further increase in the surface concentration of Cu and a corresponding decrease in the rate of hydrogenolysis of ethane. No shifts of the absorption bands in the Cu and Ru XPE spectra were observed, but the conclusion[95] that electronic interactions between Cu and Ru are negligible does not seem justified.

A possible explanation of the reported effects is the following. Intermediate particles bound to several Ni atoms on the surface (i.e. bound to the cluster) are formed during the hydrogenolysis of C_2H_6. The addition of Cu lowers the probability of finding a cluster of several Ni (Ru,Os) atoms on the surface (geometric effect), and the rate of hydrogenolysis decreases. These intermediates are not formed during the dehydrogenation of cyclohexane, and therefore the rate of this reaction remains unaffected by the addition of copper over a wide range of composition.

This explanation is inconsistent with some of the considerations outlined above. Thus it has long been known that the adsorption of cyclohexane on Ni is accompanied by the formation of 8–12 bonds per molecule, i.e. it requires the presence of a much larger cluster of Ni atoms than does the conversion of a C_2H_6 molecule[96]. Hence the rate of dehydrogenation (or hydrogenolysis) of cyclohexane should be much more sensitive to the concentration of copper in the nickel than the rate of hydrogenolysis of ethane (if the geometric factor is predominant). In reality the situation is complicated by the possibility of changes in composition and in structure of the surface during the reaction, by the formation of carbonaceous surface structures, etc. Thus the problem of selectivity changes in the course of the reaction is still unsolved.

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Though the problems presented by catalysis by supported metal crystals appear unrelated at first sight they have some important features in common, and progress in our understanding of any one of these problems can be expected to lead to progress in all directions.

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Zelinskii Institute of Organic Chemistry
of the USSR Academy of Sciences, Moscow