

Periodic Variations in the Catalytic Properties of Metals

THE INFLUENCE OF SOLID STATE PARAMETERS ON ADSORPTION AND CATALYSIS

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Of the one hundred or so elements in the Periodic Table no less than seventy-five are metals, but of these only the twelve in Groups VIII and IB have important catalytic properties. The marked changes in these properties on proceeding either vertically or horizontally through the groups is discussed in terms of the periodic variation of the solid-state properties of the metals.

It is now well established that the occurrence of significant and useful catalytic properties is largely confined to the elements lying in Groups VIII and IB of the Periodic Table. Other elements of the transition series are able to act catalytically, but because of the great thermochemical difficulty of reducing them to the metallic state, and of keeping them reduced, they do not find any practical applications. Metals which have either no *d*-electrons or which have only filled *d*-electron shells, while sometimes thermochemically suitable, are generally catalytically inactive, and catalysis (particularly of hydrogenation and related reactions) has therefore come to be particularly associated with the presence of unpaired *d*-electrons in the metal.

There are, however, many large and important differences between the twelve metals constituting Groups VIII and IB: to facilitate discussion we will subdivide the twelve metals as follows:

- (1) The Group IB metals (coinage metals):
Cu, Ag, Au.

- (2) The first row Group VIII metals (base metals): Fe, Co, Ni.
(3) The second and third row Group VIII metals (platinum group metals): Ru, Rh, Pd, Os, Ir, Pt.

Comparison of Groups VIII and IB

There are dramatic differences between the catalytic properties of the Group IB metals and those metals lying adjacent in Group VIII: these differences are particularly marked with hydrogenation and similar reactions. Silver and gold are totally unable to activate hydrogen and hence to catalyse reactions involving hydrogen, while their immediate neighbours to the left, palladium and platinum, are among the best known hydrogenation catalysts. This simple observation constitutes the most vivid possible demonstration of the existence of an *electronic factor* in catalysis, since geometrically speaking there is very little difference between palladium and silver, or between platinum and gold (see Table I). Their electronic properties (magnetic susceptibility, electrical conductivity, etc.) are of course substantially different; the Group VIII metals having incomplete *d*-electron bands are paramagnetic, while the Group IB metals having no unpaired *d*-electrons are diamagnetic (see Table II). The presence of unfilled *d*-electrons is essential to hydrogen chemisorption, as they stabilise an intermediate weakly-held form without which dissociation cannot occur.

A similar but less marked difference in catalytic properties exists between nickel

and copper. Although nickel is generally much superior, copper is not without some modest properties as a hydrogenation catalyst, being particularly attractive for the selective hydrogenation of alkynes and diolefins (1). The reason for the slight activity of copper has been a matter of debate for many years and no firm conclusion has been arrived at. It is possible that the *d*-electrons in copper are more readily thermally excited to *sp*-states than those of silver and gold, and that as before the resulting unpaired *d*-electrons are responsible for catalytic activity.

The Group IB metals are more active than their Group VIII neighbours in the rare cases where the metal is required to act as an electron-donor, as for example in the case of the decomposition of hydrogen peroxide (2). Silver has an important role to play as a controlled oxidation catalyst, and is used on a large scale for the oxidation of ethylene to ethylene oxide and of methanol to formaldehyde. Copper is too easily oxidised to be a possible catalyst, and gold is so noble that it is unable even to chemisorb oxygen. The Group VIII metals usually give only complete oxidation.

Comparison of the Base Metals with the Platinum Group Metals

It is now desirable to compare the differences in physical and catalytic properties observed on moving vertically through each sub-group of Group VIII. The base metals differ from the platinum group metals in many of their physical and chemical properties. The lanthanide contraction is responsible for the close similarity in the atomic and metallic radii of vertically adjacent pairs of the platinum group metals, and this is substantially responsible for other similarities, for example, in latent heats of sublimation and in melting points (see Table III) and in mechanical properties. All the metals of the second and third sub-groups are face-centred cubic in structure, but those in the first sub-group are either body-centred cubic or close-packed hexagonal (see Table I).

Table I
Crystal Structure, Metallic Radius and Density of the Elements of Groups VIII and IB

b.c.c. = body-centred cubic
c.p.h. = close packed hexagonal
f.c.c. = face-centred cubic

Fe b.c.c. 1.24Å 7.87 g/cc	Co f.c.c. 1.25Å 8.90 g/cc	Ni f.c.c. 1.24Å 8.90 g/cc	Cu f.c.c. 1.27Å 8.96 g/cc
Ru c.p.h. 1.32Å 11.90 g/cc	Rh f.c.c. 1.34Å 12.44 g/cc	Pd f.c.c. 1.37Å 12.02 g/cc	Ag f.c.c. 1.44Å 10.49 g/cc
Os c.p.h. 1.33Å 22.48 g/cc	Ir f.c.c. 1.35Å 22.5 g/cc	Pt f.c.c. 1.38Å 21.45 g/cc	Au f.c.c. 1.44Å 19.3 g/cc

There is also a related sharp break between the first and second row elements with regard to electronic properties. The base metals are ferromagnetic while the platinum group metals are paramagnetic (see Table II): the base metals are readily oxidised and corroded (and their compounds are correspondingly more difficult to reduce to the metallic state), and have lower electrode potentials, than the platinum group metals. This has important practical consequences in catalyst preparation, since for example nickel oxide is not easily reduced to the metal while the oxides of palladium and platinum can be reduced to the corresponding metals by hydrogen under ambient conditions. The significant differences in the chemistry of the elements of Group VIII also have repercussions on preparative procedures for catalysts. Thus there are no palladium or platinum analogues of the simple nickel salts such as $\text{Ni}(\text{NO}_3)_2$ and NiSO_4 , while hydrated nickel chloride, freely water soluble, contrasts with palladium chloride, which is anhydrous, polymeric in structure and virtually insoluble in water.

The differences between the catalytic properties of the base metals and the platinum group metals are too numerous and well-known to warrant a detailed exposition. The latter are generally superior to the former as

Table II
Magnetic Character and Mass Magnetic Susceptibility (c.g.s. units $\times 10^6$) of the Elements of Groups VIII and IB

Fe ferro- magnetic —	Co ferro- magnetic —	Ni ferro- magnetic —	Cu dia- magnetic -0.09
Ru para- magnetic +0.50	Rh para- magnetic +1.11	Pd para- magnetic +5.4	Ag dia- magnetic -0.20
Os para- magnetic +0.05	Ir para- magnetic +0.15	Pt para- magnetic +1.10	Au dia- magnetic -0.15

catalysts for hydrogenation and related reactions, although the cost differential (about 20 between nickel and palladium) sometimes counteracts the activity difference. For this reason also iron is widely used in ammonia synthesis and decomposition, although the more costly ruthenium is in fact more efficient. The superiority of platinum as a hydrogenation-dehydrogenation catalyst, however, determines its selection for petroleum reforming operations, notwithstanding the cost factor. The platinum group metals are the undoubted choice for oxidation processes such as the hydrogen-oxygen reaction, complete hydrocarbon combustion and ammonia oxidation, where base metals would be rapidly oxidised and inactivated.

Catalytic Properties of the Platinum Group Metals

Although the metals of the platinum group distinguish themselves from all others in terms of their catalytic abilities (6, 7) there are nevertheless important differences between the various members of the group. Specific points of difference have been described previously (3) and it is only necessary to mention a few examples here. Ruthenium is very much less active than palladium for the reduction of aromatic nitro-groups, while the reverse is true for carbonyl group reduction. The reduction of

methylene groups in certain steroids is more stereoselective when iridium is the catalyst than when platinum is used (4). As a final example, palladium is more active than rhodium for the hydrogenolysis of substituents (for example, alkoxy groups and halogen atoms) from aromatic rings (5). Attempts to rationalise effects of this kind have only been made in very limited contexts, the difficulty being the lack of adequate knowledge concerning metals other than palladium and platinum.

It is instructive to seek the origin of these differences in catalytic behaviour. The different crystal habits (Table I) may have some effect, but it is probably not large. There has been much discussion over a protracted period on the relation between the catalytic properties and the bulk properties of metals (6, 7, 8). Although catalytic effects must result from the physico-chemical properties of surface atoms, there are grounds for hoping that these, themselves not easily measurable, will reflect the more easily measurable bulk properties.

An important effect in determining catalytic activity is undoubtedly the strength of adsorption of intermediate species. For optimum catalytic performance there is required maximum coverage by species of minimum adsorption energy. With metals to the left of Group VIII activity is lower because the adsorption energy is too high; to the right it is lower because the adsorption energy is too small to maintain adequate surface coverage. The precise position of the activity maximum depends on the nature of the reaction, as is demonstrated in Figs 1 and 2. The view has often been expressed that the strength of chemisorption bonds parallels the strength of the metal-metal bond in the solid, and so correlations have been sought between catalytic activity and latent heat of sublimation (9) or other physical properties (6) which should reflect the metal-metal bond strength and which vary periodically with increasing atomic number. Unfortunately the physical properties in question divide themselves into two groups, one of which indicates maximum

cohesive strength in Groups V or VI of the Periodic Table, and the other of which indicates maximum cohesive strength in Group VIII (6). The former group of properties involves phase changes (sublimation, melting, etc., see Table III) while the latter does not (density, metallic radius, etc., see Table I) and is therefore thought to be more reliable as a guide to cohesive strength.

Although these properties vary rationally and periodically with increasing atomic number, because of the difficulties outlined above it may be preferable for the present to seek only to correlate catalytic properties with position in the Periodic Table. In a sense this is avoiding the main issue, but if some trends can be discerned as the electron/atom ratio changes then some rationalisation of catalytic phenomena may be hoped for.

The limited success that quantitative correlations with physical properties enjoyed is due in part to the different physical forms in which the metals have been used. If, however, attention is concentrated upon those catalytic properties which are substantially indepen-

dent of the physical form of the catalyst then some measure of order is apparent. Detailed study of the hydrogenation of olefins, diolefins and alkynes catalysed by all the Group VIII metals has revealed a consistent pattern of behaviour which correlates qualitatively with the known stabilities of organometallic olefin complexes; this work has been reviewed in detail elsewhere (10). A larger challenge is, however, presented when the hydrogenation of other functional groups is attempted on a comparative basis, because the important and useful selectivity consideration is frequently absent and reliance has to be placed on qualitative rate measurements. Nevertheless certain regularities of behaviour are emerging, and these are worth sketching in outline.

Hydrogenation of the Aromatic Ring

Although all the platinum group metals are in some measure active for the gas-phase reduction of aromatic hydrocarbons, significant differences appear when they are used under mild conditions in liquid-phase reduc-

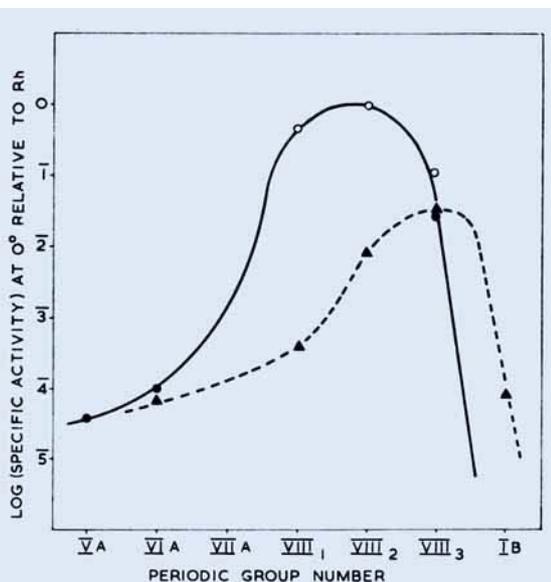


Fig. 1 Periodic variation in the activity of transition metals for ethylene hydrogenation (data from reference 6)
 Δ first row metals ○ second row metals
 ● third row metals.

Table III
Latent Heat of Sublimation and Melting Point of the Elements of Groups VIII and IB

Fe 99 kcal/g atom 1540°C	Co 102 kcal/g atom 1493°C	Ni 101 kcal/g atom 1455°C	Cu 81 kcal/g atom 1083°C
Ru 155 kcal/g atom 2400°C	Rh 133 kcal/g atom 1966°C	Pd 89 kcal/g atom 1554°C	Ag 68 kcal/g atom 960°C
Os 187 kcal/g atom 3045°C	Ir 158 kcal/g atom 2454°C	Pt 135 kcal/g atom 1773°C	Au 84 kcal/g atom 1063°C

tion. Palladium is inactive, whereas both rhodium and ruthenium are active: unfortunately it is not possible to quantify this statement because of the different kinds of catalyst that have been used. The aromatic ring is expected to adsorb parallel to the surface, and the bond probably involves partial donation of the delocalised π -electrons of the ring to the metal (11). Hence naively the lower the electron/atom ratio, the stronger the adsorption is expected to be. We therefore conclude that palladium is inactive because it does not adsorb the aromatic ring sufficiently strongly. It is significant that compounds such as phenol and aniline, having substituents which donate electrons to the ring and which hence would be expected to adsorb more strongly, are more reactive than benzene when palladium is used as catalyst.

Hydrogenation of the Carbonyl Group

Aromatic aldehydes and ketones are readily hydrogenated in the presence of palladium catalysts while the corresponding aliphatic compounds are unaffected under mild conditions. Now because of electromeric effects, the carbonyl group in aromatic compounds will have a greater electron density than in aliphatic compounds. Hence adsorption of the carbonyl group on palladium would seem to involve electron donation from this group to the metal, and the low reactivity of aliphatic carbonyl compounds is probably due to insufficiently strong adsorption. If this is so, we may predict that on moving to rhodium and thence to ruthenium, that is, with decreasing electron/atom ratio, the adsorption and hence the reactivity of aliphatic carbonyl compounds should increase, and qualitatively this is what is observed.

The activity of the second row metals for hydrogenation of aromatic nitro-compound conversely increases with increasing electron/atom ratio. We therefore infer that adsorption of the nitro-group is either too strong on ruthenium (which is inactive) or alternatively that adsorption involves electron donation

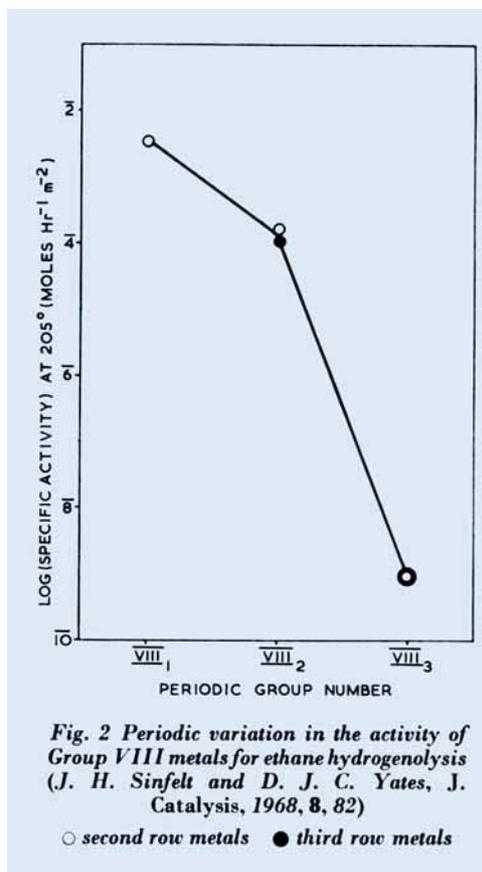


Fig. 2 Periodic variation in the activity of Group VIII metals for ethane hydrogenolysis (J. H. Sinfelt and D. J. C. Yates, J. Catalysis, 1968, 8, 82)

○ second row metals ● third row metals

from the metal to the nitro group, the inactivity of ruthenium being due to too weak adsorption of the reactant. We cannot distinguish these possibilities without further experimental work.

Conclusions

On passing along any row of the Group VIII metals from left to right, the increasing electron/atom ratio has the effect of decreasing the strength of metallic bonding since the number of unpaired electrons is falling. Hence also the concentration of valency electrons at the surface is falling, and this means decreasing strength of adsorption for those species where the metal donates electrons to the adsorbate. Catalytic activity across the row may either increase or decrease depending on where the optimum adsorption strength occurs. A knowledge of the sense of

the activity change with increasing electron/atom ratio can give valuable clues to the reaction mechanism and can assist the selection of catalysts of optimum activity for particular reactions. For example, binary alloys of metals having activities possibly superior to those of pure metals may be selected on this basis.

References

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High Purity Palladium Brazing Alloys

MULTI-STAGE JOINING IN THE MANUFACTURE OF THERMIONIC VALVES

The manufacture of special purpose thermionic valves operating at relatively high temperatures and under conditions of high vacuum necessitates the use of brazing alloys specifically suited to these requirements. Such alloys must be free from impurities that might hinder wetting and flow of the molten brazing material, must have low vapour pressures at high service temperatures, high melting points and, where needed, good mechanical properties at high temperatures.

While the well known silver-copper eutectic alloy melting at 778°C can satisfy a good many of these requirements when produced under careful conditions, alloys containing palladium show distinct advantages in terms of both vapour pressure requirements and mechanical properties, while also giving improved wetting characteristics on molybdenum, tungsten and nickel alloys. In addition they offer reduced risk of failure of the joints due to intergranular penetration.

Pallabraz High Purity Brazing Alloys		
Alloy	Composition	Melting range °C
Pallabraz 810	5 Pd-Ag Cu	807-810
Pallabraz 840	10 Pd-Ag Cu	830-840
Pallabraz 850	10 Pd-Ag Cu	824-850
Pallabraz 880	15 Pd-Ag Cu	856-880
Pallabraz 900	20 Pd-Ag Cu	876-900
Pallabraz 950	25 Pd-Ag Cu	901-950
Pallabraz 1010	5 Pd-Ag	970-1010
Pallabraz 1090	18 Pd-Cu	1080-1090
Pallabraz 1225	30 Pd-Ag	1150-1225
Pallabraz 1237	60 Pd-Ni	1237

The Pallabraz range of high purity palladium brazing alloys developed by Johnson Matthey was described in this journal some years ago by M. H. Sloboda (*Platinum Metals Rev.*, 1963, 7, 8), but a revised Data Sheet just published by the company brings up to date the detailed properties and uses of these alloys. As will be seen from the table, a range of brazing materials is available to provide melting points spaced at convenient intervals so that complex assemblies can be fabricated by the step-by-step technique.