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Influence of Metallic Additives on the Reduction of Solid Oxides

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The present review deals with one type of topochemical heterogeneous-catalytic reaction—the reduction of solid oxides by gaseous reducing agents (chiefly molecular hydrogen) in the presence of small quantities of metallic additives. Experimental data on the influence of these additives on the reduction of various oxides have been systematised, and the general regular features characteristic of these processes have been formulated. These regular features have been interpreted from the viewpoint of an electronic-chemical reduction mechanism. Methods for the practical utilisation of these reactions have been indicated. The bibliography contains 34 references.

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I. INTRODUCTION

Reactions involving the reduction of metal oxides by gaseous reducing agents (hydrogen, carbon monoxide, etc.) form the basis of many metallurgical processes, are widely employed in preparative inorganic chemistry, and are used for the preparation of various metallic and oxide catalysts.

Comparatively recently it was found that the rates of these processes are increased appreciably if the oxide being reduced contains a very small quantity of a foreign metal, such as platinum or palladium; in the presence of these additives, the temperature at which the reduction can be carried out is reduced considerably. Thus the addition of only 0.1 wt. % of metallic platinum to V_2O_5 lowers the temperature of the start of the reduction of V_2O_5 by molecular hydrogen by 180 deg[1].

An important characteristic feature of these systems is that the metallic additive under the conditions of the reaction does not form chemical compounds or solid solutions with the original oxide or the products of its reduction—it forms a distinct (usually highly dispersed) phase, separated by an interface from the phase of the oxide being reduced and its reduction products. The thermodynamic characteristics of the original oxide remain unchanged when the metallic additive is added. For example, the energies of the bonds formed by oxygen with pure V_2O_5 and with V_2O_5 containing 0.1 wt. % Pt are identical; this was proved experimentally by study of the adsorption-chemical equilibria, the temperature dependence of the equilibrium pressure of oxygen over V_2O_5,[2] and the rate of isotopic exchange of oxygen with V_2O_5.[3]

Thus the metallic additive, without influencing the thermodynamics of the reduction, increases its rate considerably, that is it catalyses the reduction. Since the catalyst (the metallic additive) and the reagents (the oxide being reduced, and the gaseous reducing agent) are in different phases, reactions of this type represent a unique form of heterogeneous catalysis.

These reactions are in some respects similar to gaseous heterogeneous-catalytic reduction processes; the rates of the latter are also increased by group VIII metals, which activate molecular hydrogen and other gaseous reducing agents. On the other hand, these reactions are heterogeneous topochemical reactions, in which one solid substance (the original oxide) is converted into another (lower oxide or metal); the reactions are characterised by certain specific features (nucleus formation, autocatalysis by the solid product, etc.).

The mechanism of the reduction of oxides in the presence of metallic additives is undoubtedly extremely complex. Its study is difficult, if only because the detailed mechanisms of heterogeneous catalysis and topochemical reactions are not yet clear. Nevertheless, the detailed study of the kinetics and mechanism of these reactions is opening up extremely interesting possibilities from both theoretical and practical viewpoints.

A fairly large amount of isolated experimental facts and observations providing evidence of the marked effect of metallic additives on the reduction of oxides, chiefly by molecular hydrogen, has now accumulated. The experimental data relating to different systems, however, are scattered—they have not been summarised from a single viewpoint, and indeed they have not until now been systematised.

This systematisation is undertaken in the present review, which attempts to reveal and where possible explain various common regular features characteristic of reactions of this type, and also to indicate methods for their practical utilisation.

II. METHODS OF PREPARING CATALYSTS, AND THEIR PHYSICAL PROPERTIES

Several methods for introducing a metallic additive into oxides to be reduced are known.

(1) Impregnation of the oxide with a solution containing a compound of the metal, followed by decomposition of this compound with the formation of the metal. Usually, the powdered oxide is impregnated with a solution of a compound such as H_2PtCl_6, $PdCl_2$, $AuCl_3$, etc., after which the powder is dried and heated to temperatures which ensure formation of the metal.

(2) Deposition of the oxide and metal on an inert carrier. The metal is first deposited on the carrier (Al_2O_3, SiO_2,

etc.) by the method described above, after which the specimen is impregnated with a solution of a salt which is decomposed to give the oxide to be reduced.

(3) Mechanical mixing; a) highly dispersed metal powder, for example platinum black, is mixed with the powdered oxide, and the mixture is shaped to form tablets; b) in a variation of this method, the oxide to be reduced is mixed with a powdered carrier (Al_2O_3, $BaSO_4$, etc.) on which the metal has been deposited beforehand. In addition to these basic methods, ion exchange[4] or spraying of the metal on to oxide granules[5] are also sometimes used.

Metals deposited even in small quantities on oxides or inert carriers are present chiefly in the crystalline state, in the form of fine crystals, the dimensions and distribution of which depend on the nature of the carrier, its surface area and porosity, the method of deposition and concentration of the metal, and the conditions of treatment[6]. Electron microscopy[7] has shown that in V_2O_5.0.5% Pt specimens the discrete platinum crystals do not penetrate into the V_2O_5 lattice or distort it, but are present in contact with the oxide. The direct deposition of the metal on the oxide ensures closer contact between the catalyst and the oxide being reduced than mechanical mixing.

III. CATALYTIC ACTION OF SMALL QUANTITIES OF METALLIC ADDITIVES ON THE REDUCTION OF OXIDES BY MOLECULAR HYDROGEN

1. Reduction of Vanadium Oxides

The catalytic action of very small quantities of platinum on the reduction of V_2O_5 was first established by Il'chenko and Yuza[1], who made a detailed study of the influence of various factors on the kinetics of this reaction†. The experiments were carried out by a gradient-free stationary–circulation method (the water formed was frozen out) under conditions free from the distorting influence of the macro-factors. The platinum was introduced into the specimens by method (1): its concentration was varied from 0.0005 wt. % to 0.5 wt. %, relative to the original oxide, the specific surface of which was 4.9 $m^2\ g^{-1}$.

The accelerating effect of platinum is shown even with trace quantities (0.0005%). The reduction of pure V_2O_5 begins at 420°. The addition of platinum lowers the temperature of the start of the reaction considerably (Table 1).

X-Ray diffraction and chemical analysis of specimens of pure and platinised V_2O_5, reduced to different extents, showed that in both instances the reduction takes place in three macro-stages:

$$3\,V_2O_5 + 2\,H_2 = V_6O_{13} + 2\,H_2O\,,$$
$$V_6O_{13} + H_2 = 3\,V_2O_4 + H_2O\,,$$
$$V_2O_4 + H_2 = V_2O_3 + H_2O\,.$$

The kinetic curves for the reduction have the S-shape characteristic of autocatalysis by a solid reduction product.

The addition of platinum increases the rates of all three macro-stages, but the catalytic action of platinum is greater at low degrees of reduction. In this range, which corresponds to the conversion of V_2O_5 into V_6O_{13}, the rate of reduction of platinised specimens containing up to 0.01% Pt is proportional to the concentration of the metallic catalyst and the hydrogen pressure to the first power. Increase in the platinum concentration (C_{Pt}) leads to a change in the kinetic relationships: at C_{Pt} = 0.1% the order with respect to hydrogen becomes less than unity, and at C_{Pt} = 0.25% a saturation effect is observed—further addition of platinum does not influence the temperature of the start of the reduction (Table 1).

Table 1. Dependence of the temperature of the start of the reduction of V_2O_5 by hydrogen on the concentration of platinum (hydrogen pressure 400 mmHg).

Platinum concn., wt.%	Temperature of the start of reduction, °C
0	420
0.001	360—370
0.01	300
0.1	240
0.25	220
0.5	220

The catalytic action of platinum begins to be shown at very low degrees of reduction, when the removal of oxygen from the oxide being reduced has not led to a phase transformation. Il'chenko and coworkers[2] studied the adsorption-chemical equilibrium

$$(O) + H_2 \rightleftarrows (\ ) + H_2O,$$

with the participation of V_2O_5, where (O) denotes oxygen of the oxide, and ( ) an oxygen vacancy; the quantity of oxygen removed does not exceed that corresponding to a monolayer. It was found that the addition of platinum, without altering the equilibrium constant for this process, leads to a sharp increase in the rate of attainment of equilibrium. Similar relationships were observed for V_2O_5 on which platinum had been deposited directly and for specimens prepared by mechanical mixing of V_2O_5 with $Pt/BaSO_4$.

Platinum also has a significant effect on the regular features of nucleus formation in the reduction of V_2O_5: in the reduction of the pure oxide, the nuclei of the solid product are produced according to a power law, whereas in the presence of platinum the nuclei are formed according to a more rapid exponential law[9]. An increase in the ease of nucleus formation in the presence of platinum is also revealed in the fact that the addition of platinum leads to a sharp decrease in the duration of the induction period observed in the reduction of V_2O_5.[1]

2. Reduction of Tungsten Oxides

Khoobiar[10,11] found that platinum has a marked catalytic action on the reduction of WO_3. He established that WO_3 powder, mixed with Pt/Al_2O_3 (0.5 wt. % Pt) is reduced by molecular hydrogen even at room temperature; under these conditions, pure WO_3 is not reduced and reacts with H_2 at temperatures above 400°.

A detailed study of the influence of added platinum on the reduction of WO_3 was made by Benson and coworkers[12], who used a gas-volumetric method. Most of their work was carried out with specimens obtained by grinding WO_3 powder with platinum black: metal concentration 2.5 wt. %, specific surface of metal 23 $m^2\ g^{-1}$, specific surface of WO_3 11.1 $m^2\ g^{-1}$ and 17.4 $m^2\ g^{-1}$.

† Even earlier, Yuza and Roiter[8] found that the rate of reduction of V_2O_5 by hydrogen was increased considerably after the V_2O_5 had been melted in a platinum crucible.

In the reaction of WO_3 with hydrogen, water was not liberated, and a pale-blue powder with the composition $H_{0.35}WO_3$ (the hydrogen analogue of the tungsten bronzes) was formed. Pure WO_3 begins to absorb hydrogen very slowly at 435°; in the presence of platinum the dry oxide begins to be reduced at 105°, and a specimen covered beforehand with a monolayer of water begins to be reduced at room temperature. Thus the catalytic activity of platinum is increased considerably in the presence of water adsorbed on the oxide surface.

The accelerating influence of platinum is more marked, the closer the contact between its micro-crystals and the surface of the oxide being reduced. Thus the rate of reduction is greater when the metal is deposited on WO_3 by impregnation than when the tungsten(VI) oxide is ground with platinum black, and much greater than when WO_3 powder is simply ground with platinum. An interesting feature is that the preparation of WO_3 specimens in platinum crucibles leads to an appreciable decrease in the temperature of the start of the reduction of this oxide, compared with specimens prepared in porcelain crucibles [13]. An analogous effect was observed for V_2O_5 (see p. 86).

Hegedüs and coworkers [13] made a detailed study of the influence of various metallic additives on the reduction of WO_3. The specimens were prepared by method (1) and contained 0.5 wt. % metal relative to W; the studies were made by a thermogravimetric method (the specimens were heated in a stream of gaseous reducing agent with continuous increase in temperature), with X-ray diffraction study of the solid products. Experimental data characterising the catalytic action of palladium, platinum, and osmium are given in Table 2.

Table 2. Influence of metallic additives on the reduction of WO_3 by a 30% H_2 + 70% N_2 mixture [13].

Additive	Temp. of the start of reduction, °C	Temp. at which $WO_{2.88}$ is formed, °C	Temp. corresponding to the end of the reaction, °C
Pd	284	345—529	768
Pt	290	351—527	779
Os	350	446—546	794
Pure WO_3	430	530	800

A strict quantitative comparison of the catalytic action of the different metals on the basis of Hegedüs' data [13] is difficult, since their surface concentrations might have been different, but it is clear that the order of activities of the additives is: Pd > Pt > Os. Neugebauer and coworkers [14] found that the activity of added palladium in the reduction of WO_3 is particularly high in the presence of water.

Unfortunately, the experimental data given by Hegedüs and coworkers [13] were not systematised and discussed. Analysis of these data led us to the following conclusions.

1. The accelerating action of the additives decreases with increase in the degree of reduction of WO_3 (Table 2). The temperature of the start of the reaction and the temperature of the start of the conversion of WO_3 into the blue β-oxide of tungsten ($WO_{2.88}$) is lowered appreciably in the presence of metals, whereas the temperature at which this change is complete is approximately the same as in the reduction of pure WO_3. Additives also have comparatively little influence on the temperature corresponding to the completion of the reduction.

2. Hegedüs and coworkers [13] also studied the influence of various other additives, in particular Hg, Al, Sn, Pb, Sb, and Bi, on the reduction of tungsten(VI) oxide. The additives were present in the original WO_3 specimens as the metal chlorides. The true chemical state and concentration of these additives under the conditions of the reaction were unknown; allowance must be made for the fact that the chlorides of these metals are volatile, and the metals themselves readily fusible, so that most of them (Hg, Sn, Pb, and Bi) are in the liquid state at the temperature of the start of the reduction. These additives (apart from Bi) do not accelerate the reduction of WO_3, and even retard it (Table 3).

Table 3. Influence of added readily fusible metals on the reduction of WO_3 by a 30% H_2 + 70% N_2 mixture [13].

Additive	Temp. of the start of reduction, °C	Temperatures at which $WO_{2.88}$ is formed, °C
Hg	433	521
Al	481	552
Sn	469	539
Pb	476	535
Sb	439	504
Bi	313	440—575
Pure WO_3	430	530

3. Reduction of Molybdenum Oxides

The influence of various metallic additives on the reduction of MoO_3 was studied by Hegedüs and coworkers [15], who used the same procedure as in the study of the reduction of WO_3. [13] The regular features observed in this instance were completely analogous to those found for the reduction of tungsten(VI) oxide. The addition of noble metals increases the rate of reduction of MoO_3 (Table 4), the catalytic activity decreasing in the order: Pd > Pt > Ag > Os. The addition of readily fusible metals (Hg, Al, Sn, Pb, Sb, or Bi) has little influence on the reduction of MoO_3.

4. Reduction of Nickel(II) Oxide

Verhoeven and Delmon [5] studied the reduction of NiO by hydrogen at 210–220° in the presence of added platinum, palladium, copper, gold, and silver. It was found that the first three metals increase the rate of the process considerably, and decrease sharply the duration of the induction period. The kinetic curves for the reduction are S-shaped, as in the reduction of pure NiO, that is the autocatalytic action of the solid product—metallic nickel—is also shown in the presence of the additives.

Added gold and silver have little influence on the rate of reduction of NiO, and added cadmium has a slight retarding action at 277–293°.

The accelerating action of palladium and platinum on the reduction of NiO by hydrogen was also demonstrated by Nowak and Koros [16]. In their experiments, both the metal and the oxide being reduced were deposited in small quantities on aluminium oxide. The catalytic activity of palladium was greater than that of platinum.

5. Reduction of Iron Oxides

Sancier and Inami[4] studied the influence of added palladium, platinum, copper, gold, and a palladium–gold alloy on the reduction of Fe_2O_3 (and Fe_3O_4) by hydrogen at 500°; the reaction rate was measured by the EPR method. The specimens for reduction were prepared by various methods: by depositing the metal and the oxide on Al_2O_3 or SiO_2 by impregnation; by mechanically mixing Fe_3O_4 and a carrier containing the metal additive; and by using a molecular sieve containing the metal cation and iron ions. The following order of catalytic activities was found: Pd > Pt > Cu ~ Pd–Au > Au.

Table 4. Influence of metallic additives on the reduction of MoO_3 by a 30% H_2 + 70% N_2 mixture[14].

Additive	Temp. of the start of reduction, °C	Temperatures at which MoO_2 is formed, °C
Pd	185	—
Pt	260	—
Ag	420	585—625
Os	500	625—645
Pure MoO_3	510	645

The activity of Pd–Au alloys containing 20 at. % and 60 at. % Au was found to be lower than that corresponding to the volume concentration of Pd; this was attributed to an increase in the concentration of gold on the surface compared with the volume. The rates of reduction of specimens obtained by the joint deposition of catalyst and oxide being reduced, and also by ion exchange, were greater than that for mechanical mixtures. According to Samchenko and Rusov[17], small quantities of platinum (0.01 wt. % and 0.1 wt. %) produce a marked increase in the rate of reduction of iron oxides (also containing K_2O, Al_2O_3, CaO, SiO_2, etc.) by a nitrogen–hydrogen mixture‡. At 450° and a pressure of 60 atm, the time required for a given degree of reduction to be achieved is much shorter in the presence of platinum. According to the data of Murata and Kasaoka[18], added copper increases the rate of reduction of Fe_2O_3 and Fe_3O_4 below 250°.

6. Reduction of Copper Oxides

The accelerating action of platinum on the reduction of copper oxide films was detected by Vorontsov and Koshkina[19]. In the absence of catalyst these films are reduced completely in 97 min at 200°, whereas in the presence of platinised platinum the reaction is complete in 7 s. In the presence of the catalyst the process is rapid even at 40°.

IV. GENERAL REGULAR FEATURES AND MECHANISM OF ACTION OF METALLIC ADDITIVES ON THE REDUCTION OF OXIDES BY MOLECULAR HYDROGEN

In the analysis of the above experimental facts, we observed various regular features characteristic of these processes.

1. An extremely high catalytic activity in the reduction of a given oxide is shown by palladium and platinum (usually, Pd > Pt); copper, and also osmium, are less active; silver and gold have little activity; and readily fusible metals—cadmium, mercury, lead, tin, and aluminium—are inactive.

2. The accelerating influence of metallic additives is particularly marked in the initial period of reduction, at low degrees of reduction; the active catalysts in a number of instances decrease the temperature of the start of the reaction by hundreds of degrees.

The action of the additives is also shown at high degrees of reduction, but to a smaller extent. If the reaction is carried out at a sufficiently high temperature, it is possible to achieve a greater degree of reduction in the presence of the metallic catalyst than in the absence of the additive (within the limits allowed by thermodynamics).

3. In those instances where the reduction of the pure oxide is autocatalytic, the autocatalytic action of the solid product is usually preserved in the presence of the additive.

4. Metallic additives decrease sharply the duration of the induction period and apparently alter the kinetics of nucleus formation.

5. The catalytic action of the additives (for very small quantities) is proportional to the metal concentration; at sufficiently high concentrations, a saturation effect is observed—further addition of metal has little influence on the course of the process.

6. The catalytic activity of a metal with respect to the reduction is greater, the closer its contact with the oxide being reduced and the greater the degree of dispersion. The direct deposition of a catalyst on the oxide being reduced gives better results than mechanical mixing. Nevertheless, the accelerating action of palladium and platinum is also shown in instances where the microcrystals of the oxide being reduced and the additive, deposited on an inert carrier, are separated in space.

7. The catalytic action of metallic additives is increased in the presence of water (this conclusion was reached by a number of authors[12,14]).

These regular features can be explained on the basis of the electronic-chemical theory of catalysis and reduction, proposed by Roiter[8] and developed by a number of authors[1,7,20].

According to this theory, the limiting stage of the reduction of an oxide by molecular hydrogen§ is usually the donor process of electron transfer from the adsorbed molecules of reducing agent (H_2) to the solid oxide; this process leads to a decrease in the oxidation state of the cations of the oxide and the formation of positive hydrogen ions, which subsequently react readily with negative oxygen ions with the formation of water.

If the oxide is in contact with micro-crystals of a metallic additive able to bring about the specific activation (ionisation) of hydrogen, the transfer of electrons from H_2 to the oxide is greatly facilitated, so that the rate of the overall reduction is increased.

In fact, the above order of decreasing catalytic activity of metallic additives with respect to the reduction of oxides agrees qualitatively with their ability to activate molecular hydrogen. Palladium and platinum adsorb hydrogen rapidly even at low temperatures and can dissolve hydrogen[21]; these metals are extremely active catalysts for

‡ This process gives the industrial iron catalyst for the synthesis of ammonia ("SA-1" grade contact catalyst).

§ It is assumed that the reduction is a quasi-steady-state reaction[22].

various gaseous reactions involving H_2 [23] and have the lowest overpotential for the cathodic liberation of hydrogen[24]. Copper has a lower catalytic activity with respect to gaseous reactions involving H_2, and silver and gold have little catalytic activity in these reactions[23]. Metals such as cadmium, mercury, aluminium, bismuth, lead, and tin have little activating effect on molecular hydrogen (very high overpotential for the cathodic liberation of hydrogen; low catalytic activity with respect to reactions involving H_2 [24]). It should also be borne in mind that the metals of this last group are readily fusible, and at the temperatures of the start of the reduction of oxides difficult to reduce (MoO_3, WO_3) most of them are in the liquid state. The liquid metal may flow over the surface of the oxide, blocking it and thus hindering the reaction of the oxide with the gaseous reducing agent; this explains the slight retarding action of these additives on the reduction of MoO_3 and WO_3 (pp. 48 and 49).

In the reaction of molecular hydrogen with Pd or Pt, dissociative adsorption takes place, and the adsorbed species exhibit surface mobility. Among the transition metals, the platinum metals have the lowest heats of chemisorption of hydrogen, that is the lowest metal–hydrogen bond strength[21]. According to Aston[25], hydrogen adsorbed on platinum is mobile at 7° and above; hydrogen dissolved in palladium is also mobile over a wide temperature range. It is natural to assume that hydrogen adsorbed on Pd or Pt can migrate from the palladium or platinum centres to the regions of the oxide in contact with these centres; if the micro-crystals of the metal and the oxide being reduced are deposited on the same inert carrier (for example Al_2O_3) and are at a certain (small) distance from one another, the hydrogen first migrates to regions of the carrier adjoining the metal and then to the oxide being reduced¶.

The possibility of surface diffusion in this way is proved by a number of experimental facts. It was established[26] that in the adsorption of hydrogen from solution on Pd/Al_2O_3 and Pt/Al_2O_3 specimens with a low concentration of metal (up to 1 wt. %), the number of hydrogen atoms corresponding to one metal atom at 25° is several times greater than unity. Since hydrogen is not adsorbed on the pure carrier, the only explanation for this result is that the hydrogen migrates from the palladium or platinum centres on to the carrier. An analogous interpretation of their results was put forward by Robell and coworkers[27], who showed that in the presence of small quantities of platinum (0.2% and 1%) the rate and extent of the adsorption of hydrogen and deuterium on carbon increase considerably. A similar result was previously obtained by Frumkin and Burstein[28]. The ability of hydrogen adsorbed on platinum to undergo surface diffusion is also indicated by the fact that small quantities of deposited platinum actively catalyse the exchange of deuterium and the hydrogen of the surface OH groups of aluminium oxide[29].

It is suggested that the increased rate of reduction of oxide containing adsorbed water in addition to platinum is due to an increase in the rate of diffusion of hydrogen, brought about by water, probably as a consequence of the formation of hydroxonium ions[12].

It is quite understandable that the closer the contact between the micro-crystals of the metallic additive and the granules of the oxide being reduced, the greater the ease of electron transfer from hydrogen to the oxide being reduced, through the metallic catalyst, on which hydrogen is ionised, and the greater the ease of diffusion of hydrogen from the palladium or platinum centres to the oxide surface.

In the initial period of the reduction, when the metallic catalyst is in direct contact with the oxide being reduced, the catalytic action of the metallic additive is naturally greatest and involves primarily a marked decrease in the temperature of the start of the reaction and a sharp increase in the initial rate of reduction. This effect is greater in the reduction of oxides difficult to reduce (V_2O_5, MoO_3, WO_3), for which the temperature of the start of the reaction is decreased by hundreds of degrees†.

The higher the concentration of additive, the greater the increase in the rate of activation of hydrogen and hence of the overall process. When a definite concentration of catalyst has been reached [for platinised vanadium(V) oxide this concentration is about 0.1–0.25%], the rate of the donor stage is increased to such an extent that it ceases to be the limiting stage. The slow stage of the reaction is then another process, probably diffusion in the solid phase or crystal-chemical transformations, since at increased concentrations of additive the reaction takes place at a low temperature. The presence of a metallic additive does not influence the rates of these processes, so that further increase in the concentration of catalyst does not lead to an additional increase in rate (saturation effect)[20].

Since the gaseous reducing agent is activated on the surface of the micro-crystals of the additive, the points of contact between it and the oxide being reduced become centres for the rapid production and growth of nuclei of the new phase. As a result, in the presence of active metallic catalysts there is a sharp decrease in the duration of the induction period and a change in the kinetics of nucleus formation, as observed in the reduction of V_2O_5.[9]

With increase in the degree of reduction of the oxide, the micro-crystals of the catalyst (Pd or Pt centres) are isolated to an increasing extent from the original oxide by a layer of solid reaction product—a lower oxide or metal. The catalytic action of the additive is also shown at this stage, since the transfer of electrons from the hydrogen, ionised on Pd or Pt, to the oxide being reduced cannot be prevented by a layer of semiconducting oxide or metal surrounding the palladium or platinum centres. The catalytic action of the additive becomes weaker, however, with increase in the degree of reduction. A possible reason for this is that the diffusion of hydrogen to the reaction surface, which is steadily moving further away, is hindered.

Judging from the form of the kinetic curves, the growth of the new phase takes place on a layer of solid product already present, that is the autocatalytic action of the reduction product is preserved in the presence of the metallic additive (if this product does not form a solid

¶ A heterogeneous–homogeneous reduction mechanism, in which H atoms are transferred from the platinum or palladium surface to the gaseous phase to start a chain reaction, is unlikely. Benson and coworkers[12] demonstrated this experimentally for the WO_3–H_2 system by using γ-radiation and an electric discharge to produce H atoms specially in the gaseous phase (reduction of WO_3 at 400° was not observed).

† Oxides which are readily reduced (such as Ag_2O and MnO_2) begin to be reduced at low temperatures even without a catalyst, so that in this instance the influence of metallic additives will apparently be less marked. Unfortunately, there is as yet no direct experimental evidence for this.

solution with the original oxide). Thus in this stage, two catalysts are operating—the metallic additive and the solid reduction product. The role of the first catalyst involves the activation of hydrogen, accompanied by the transfer of electrons to the oxide being reduced; the role of the solid product involves chiefly an increase in the ease of crystallisation of the new phase at the interface between it and the original oxide. In those instances where the reduction leads to the formation of metals such as Ni, Co, Fe, and Cu, which exhibit hydrogenating power, it is possible that they themselves play some part in the activation of hydrogen.

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The study of the influence of metallic additives on the reduction of solid oxides opens up interesting possibilities for the study of the mechanisms of reactions involving solid oxides.

An example is provided by the study of the mechanism of the catalytic oxidation of hydrogen on V_2O_5 and the reduction of this oxide by hydrogen. On the basis of kinetic data it was suggested that the limiting stages of the two reactions are analogous, both involving the donor process of hydrogen ionisation with the transfer of electrons to the oxide[8]. If this suggestion is correct, we would expect that when platinum is added to V_2O_5, the rate of the limiting stage would increase, so that the rates of both the catalysis and the reduction would increase. In actual fact, in the presence of added platinum the rate of reduction of V_2O_5 increases sharply[1], and the same additive also produces a marked increase in the catalytic oxidation of hydrogen on V_2O_5.[7] It was noted above that with high concentrations of platinum (0.1–0.25%) the donor stage is no longer the slowest stage in the reduction of V_2O_5, that is, the limiting stage is replaced. Analogously, in the catalytic oxidation of hydrogen on platinised V_2O_5 at a platinum concentration of 0.1%, the rate of activation of hydrogen increases to such an extent that the slow stage of the reaction becomes the acceptor stage of activation of molecular oxygen[20]. Thus the study of the influence of metallic additives in oxides assists in the investigation of the nature of the limiting stage in heterogeneous reactions involving these oxides.

Studies of this kind are also of assistance in the investigation of the mechanism of action of bifunctional reforming catalysts of the Pt/Al_2O_3 type containing small quantities of metal. It is often suggested that a necessary stage in these processes is the surface diffusion of hydrogen, adsorbed on platinum, to the aluminium oxide regions[11]. This idea has been used to explain the increased rate of hydrogenation of ethylene on a Pt/SiO_2 catalyst mixed with Al_2O_3.[30] Experimental proof of the possibility of this migration is provided by the ease of reduction of WO_3–Pt/Al_2O_3 specimens[11].

The use of metallic additives as catalysts for the reduction of solid oxides opens up extremely important practical possibilities for increasing the activity of catalysts, as indicated in our earlier paper[1].

The reduction of oxides by gaseous reducing agents is a widely used method for preparing catalysts, including industrial catalysts. Decrease in the temperature of reduction often leads to an increase in the surface area of the catalyst as a consequence of the decrease in sintering and recrystallisation and the associated increase in the efficiency of contact. The introduction of catalytically active metal additives such as Pd or Pt into the original oxide may decrease considerably the temperature of reduction and hence lead to an increase in the total activity of the catalyst.

Small quantities of copper decrease the temperature of the reduction of Fe_2O_3 [18] and at the same time increase the activity of the reduced iron catalyst for the synthesis of hydrocarbons from CO and H_2.[31] The last effect is possibly achieved to some extent during the preparation of the catalyst.

In some instances it is extremely important that the reduction of the oxide to the metal be complete, since the presence of even small quantities of oxide in the metallic contact catalyst has an unfavourable influence on its catalytic properties. The main difficulty is that it is the last portions of oxygen which are most difficult to remove from the oxide. The introduction of catalytically active additives makes it possible to overcome this difficulty and achieve complete reduction. This technique was used by Nowak and Koros[16], who reduced NiO in the presence of small quantities of added palladium and platinum to obtain a more active and selective catalyst for the isomerisation, aromatisation, and hydrogenolysis of n-heptane.

The most successful combination is evidently that for which the additive, while increasing the rate of reduction of the original oxide, also acts as a promoter for the catalyst when it is formed. Thus Pd and Pt additives not only increase the rate of formation of the nickel catalyst mentioned above, but also apparently promote it[16]. The addition of small quantities of palladium to the zinc–chromium oxide catalyst for the preparation of alcohols from CO and H_2 leads to an increase in selectivity with respect to the formation of methanol[32].

In conclusion it may be noted that many of the regular features formulated above may be of more general significance and may also be applicable to the reduction of oxides by reducing agents other than molecular hydrogen. Thus small quantities of added palladium increase sharply the rate of the reduction of V_2O_5 by carbon monoxide: pure V_2O_5 begins to be reduced at 575°, whereas the temperature of the start of the reduction of a V_2O_5–0.1% $Pd/BaSO_4$ specimen is 25°.[33] According to the data of Blejean and coworkers[34], the addition of Pd increases the rate of the reduction of V_2O_5 by *o*-xylene and ethylene. Unfortunately, the available experimental data on the reduction of oxides by reducing agents other than H_2 in the presence of metallic additives are extremely scanty and insufficient for detailed discussion.

The systematic accumulation of new experimental data on the catalytic reduction of oxides by molecular hydrogen is also extremely desirable. Detailed kinetic studies by modern methods, combined with X-ray diffraction study and chemical analysis of the oxide being reduced, and measurement of the surface areas of the additives and the oxide, are required; in each instance it is necessary to investigate the influence of various factors (temperature, the composition of the reaction mixture, the concentration, chemical character, and physical state of the additive, the degree of reduction of the oxide, etc.) on the rate of the process. An extremely interesting unresolved problem concerns the relationship between the catalytic action of a given additive and the chemical structure of the oxide being reduced and its solid reduction products.

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