PREPARATION OF CATALYSTS BY METALLIC COMPLEX ADSORPTION ON MINERAL OXIDES

J.P. BRUNELLE

Procatalyse, Centre de Recherches Rhône-Poulenc , Aubervilliers, <u>France</u>

ABSTRACT

The usefulness of metallic complex adsorption phenomena on oxides for the preparation of dispersed metallic supported catalysts have led us to analyze phenomena which occur at the interface-oxide solution. This analysis is based on simple principles such as surface polarization of oxides versus pH and adsorption of counterions by electrostatic attraction.

The three most important parameters which seem to regulate these adsorption phenomena are : isoelectric point of the oxide, pH of the aqueous solution, and nature of the metallic complex.

This simplified approach toward adsorption phenomena is in agreement with the published results in the literature concerning the fixation of chlorometallic and amine complexes of metals belonging to 7a, 8 and 1b groups on alumina or silica carriers.

An extension of this analysis to other mineral oxides is proposed.

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1. <u>IMPORTANCE OF METALLIC CATALYSTS</u>

The importance of metallic catalysts in our economic system need certainly no longer be demonstrated today. They are involved in such diffe-- rent fields as the oil refining, automobile, petrochemical and fine chemical industries. A list of the principal processes operating with metallic catalysts will be found in table 1.

The properties of these catalysts in general and their activi.y in particular are in close relation to the state of dispersion of the active elements. This explains why three-fourths of the processes listed in table 1 use catalytic systems in which the active phase is in the form of very small crystallites of about ten angströms dispersed on the surface of a support. It is what we usually call dispersed metallic catalysts.

The metals used in these catalysts belong generally to groups 7a, 8 and 1b of the periodic table, very often such as platinum and palladium. Four supports are most often used in their preparation : alumina, silica-alumina, active carbon and molecular sieves.

It is to be noted that the Raney nickel which is still used nowadays in a lot of liquid phase hydrogenations constitutes a particular case of a dispersed metallic catalyst which is non supported.

Il we consider the tonnages of catalyst involved, the most important processes are catalytic reforming, hydrogenations of different petrochemical streams, and above all, automobile post-combustion, which represents the greatest turnover for the industry.

TABLE 1
Metallic catalysts used in oil refining, automobile, petrochemical and fine chemical industries.

	PROCESS	TYPE OF CATALYST	
		METAL	CARRIER
DISPERSE METALLIC CATALYSTS	. Auto-exhaust gases Post-combustion		Alumina or Alumina coated
	Oxydation catalysts	Pt+Pd	
	Three-way catalysts	Pt+Rh	Cordierite
	. Selective hydrogenation of :		
	Olefins streams in ethylene plants	Pd	Alumina
	Pyrolysis gasoline in ethylene plants	Pd	
	. Catalytic Reforming	Pt (+Re,Ir,Au..)	Alumina + Cl
	. Hydrocracking	Pd	Y zeolite based
	. Isomerization of :		
	Paraffins	Pt	Alumina + Cl or mordenite
	Xylenes	Pt	Alumina + Cl or Alumina-Silica
	. Dismutation of Toluene	Cu, Ni	Zeolite
	. Fine organical chemistry	Pt,Rh,Pd,Ru, Ni Raney	Charcoal
	. Off-gas Treatments	Pt,Pd	Alumina
	. Fuel Cells	Pt,Pd	Charcoal
NO DISPERSE Metallic Catalysts	. Ammonia oxidation	Pt+Rh	-
	. Selective oxidation of ethylene in ethylene oxide	Ag	α Alumina
	. Selective oxidation of methanol in formol	Ag	Carborundum

In fact, only three important processes use metallic catalysts that do not require a high dispersion of the active element: 1) ammonia oxidation to make nitric acid on a platinum-rhodium wire catalyst , 2) méthanol selective oxidation into formol and 3) ethylene selective oxidation into ethylene oxide. The latter two processes are on silver-based catalysts.

2. METHOD OF PREPARATION OF DISPERSED METALLIC CATALYSTS

Several studies (1 - 6) have shown the usefulness of metallic complexes adsorption or exchange with some surface sites of mineral supports to obtain highly metallic surfaces. It should be apparent that :
- The reduction of metallic ions adsorbed on the surface of the support must lead initially to an atomic deposit of the metal. The whole problem consists in preserving a dispersion of the metallic deposit which is as close as possible to its initial state, thus avoiding too great a crystallization of the metal during the catalyst activation.

- On the other hand, if the impregnation is made in condition where me-
  tallic precursors do not fix on the surface of the support, these pre-
  cursors are going to deposit here according to a process of crystalli-
  zation, precipitation or decomposition during the drying step . The
  size of the crystallites depends on a great number of parameters such
  as support texture, precursor solubility and drying velocity. In this
  case, crystallites smaller than 50 Å are rarely obtained.

  For instance, figure 1 enables the comparison of the mean crystallite
size of two series of platinum-silica catalysts with variable percentage of
platinum and prepared :
- either by a conventional method of impregnation without exchange from
  a chloroplatinic acid solution.
- or by tetramine platinum II cations exchange with ammonia-polarized
  surface sites of silica.
  The mean crystallite size of catalyts prepared by conventional method
varies beetween 60 and 170 Å. On the other hand, cation exchange leads to
a mean platinum crystallite size of about 10 to 20 Å, for a platinum
content varying beetween 0.4 and 5.5 wt %.

3. ADSORPTION OF ION COMPLEXES ON THE SURFACE OF MINERAL OXIDES

   Though several studies have shown the practical interest of using ad-
sorption and metallic complex exchange phenomena on mineral oxides, few
studies in fact have been carried out on this subject. Some of them deal
with the adsorption of platinum (1, 2, 4, 6, 13), palladium (3, 5, 11, 13),
cobalt, nickel, or copper (13, 14) cationic complexes on the surface of
silica or alumina supports. Some others treat the adsorption of anionic
complexes of platinum (7 - 10, 12, 13), palladium (5, 11) or other pre-
cious metals such as gold, rhodium, ruthenium, iridium (12, 13) on alu-
mina.
   Our purpose is not to describe the results obtained from these diffe-
rent studies but to treat generally the metallic complexes adsorption and
exchange phenomena on the surface of mineral oxides. In using simple prin-
ciples such as surface polarization of an oxide as function of pH and ad-
sorption of complex ions by electrostatic attraction, we try to extricate
the most important thermodynamic parameters which seem to control the rea-
lization of adsorption phenomena, and we also want to suggest the basic
principle for the choice of these parameters.
   On the other hand, we will not treat the problem of fixation of me-
tallic hydrolyzable cations (15-41). This problem, though it has often
been studied, does not yet seem to be clearly explained as the conclusions
are sometimes contradictory. The more common mechanism is hydrolytic ad-
sorption of hydrolyzable cations. This mechanism, which certainly deserves
to be carefully studied, involves a hydrolysis and not an adsorption of
the cation on the oxide.
   We will also limit our analysis to the phenomena which take place du-
ring impregnation at the interface oxide-solution without taking into
account the other phenomena which may take place afterwards during acti-
vation (reaction of the complex with the support, partial or total decom-
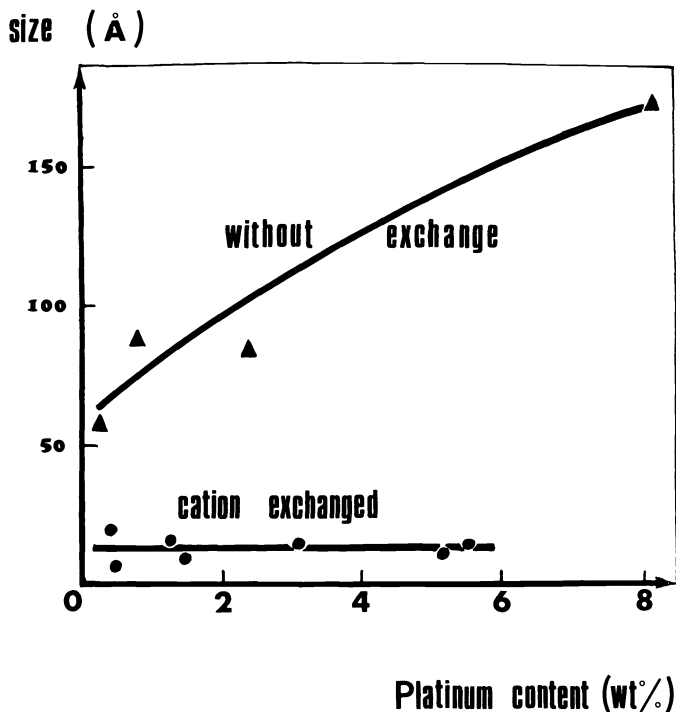position of the complex ...).

Fig. 1. Variation of the mean crystallite size vs metal content of Pt-
SiO_2 catalysts. Specific surface area of silica support = 260 m^2/g.
Activation of catalysts : drying in air at 120°C for 16 hr and reduction
in hydrogen at 410°C for 6 hr.

Finally then, we will ignore the kinetic aspect of these phenomena, even
if it is significant.

3.1. ISOELECTRIC POINT OF AN OXIDE

A particle of a mineral oxide in suspension in an aqueous solution tends
to polarize and to be electrically charged. Most oxides are amphoteric.
Thus, the nature and importance of this charge are a function of pH of the
solution surrounding the particle.

For example, in an acid medium, the particle is positively charged.
The principle of electroneutrality implies the presence of a layer of
ions with opposite charge near this particle, the two electric charges
compensating each other. If we consider a schema in agreement with the
GOUY theory, counteranions will be thus located around the particle in a
thin diffuse layer, as shown in figure 2.

Schematically, the equation of the surface polarization may be writ-
ten :

$$S-OH + H^+A^- \rightleftarrows S - OH_2^+A^-$$
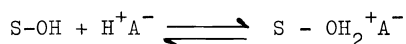
where S-OH represents a surface adsorption site and H^+A^- a mineral acid.

In a basic medium, the reverse is true. The particle is negatively

charged and is surrounded by compensating cations. The equation of the
surface polarization may be written as follows :

$$S-OH + B^+ OH^- \rightleftharpoons S-O^- B^+ + H_2O$$
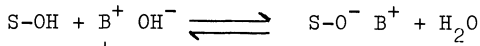
where B^+OH^- represents a base.

One conceives easily that between these two cases, a given value of pH
exists at which the particle is overall not charged. This value, which is
a characteristic of the oxide corresponds to its zero point of charge
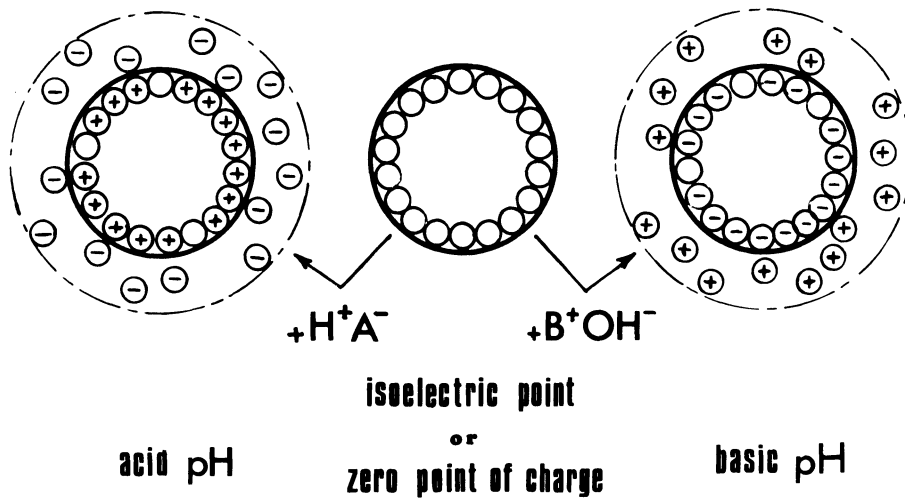(Z.P.C.) or its isoelectric point (I.E.P.S.).

+H⁺A⁻   +B⁺OH⁻

isoelectric point

or

acid pH   zero point of charge   basic pH

Fig. 2. Schematic representation of the surface polarization of an oxide
particule as a function of the solution pH

Let us now examine two methods allowing us to estimate the nature and
importance of the surface polarization of an oxide as a function of pH
of the solution in which it is dipped.

3.1.1. Electrophoresis

Electrophoresis technics enables us to measure the velocity of a charged
particle in suspension and placed in an electrical field. The electropho-
retic velocity is proportional to potential difference existing between
the opposites areas of the double layer (Zeta potential). For this reason,
it is possible to obtain through experiment the sign and the importance of
the polarization of a given oxide particle.

In order to illustrate this method, we have shown in figure 3 four
curves of Zeta potential versus pH corresponding to four different products :
a silica gel, a neodyme hydroxide gel, a titania gel and a gibbsite gel
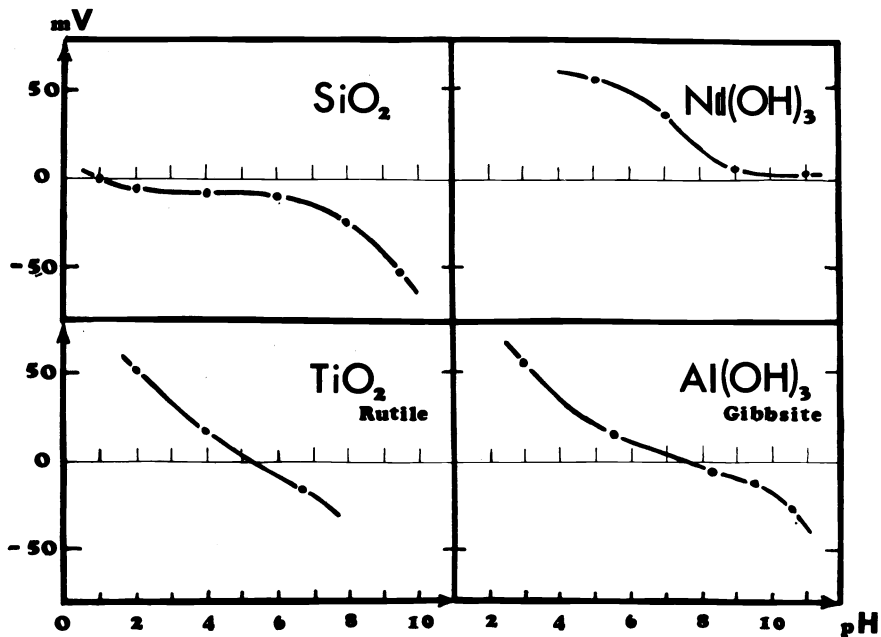(42).

Fig. 3. Various types of Zeta potential curves vs pH obtained by electro-
phoresis.

Following information can be found by examining these curves :
- The I.E.P.S. of silica, which corresponds to the cross-over point
of Zeta potential curve and pH-axis, is very low, around pH 1. This re-
sult indicates the acid and non-amphoteric type of this oxide. A negative
polarization of its surface occurs at pH higher than 1 (negative zeta poten-
tial) but becomes significant only at pH above 7. In other words, silica
may only adsorb cations, and this phenomena becomes important only at pH
above 7.
- Neodyme hydroxide has a quite opposite behaviour compared to that of si-
lica. Its I.E.P.S. is around pH 12, which is in accordance with the basic
type of this hydroxide. Its surface polarizes positively at pH below 12,
which makes possible, on the contrary as in case of silica, the adsorption
of anions on its surface.
- Titania and gibbsite gels correspond typically to amphoteric products
which results in an inversion of the polarization sign when passing from
acid to basic medium. Their I.E.P.S. are respectively equal to 5.5 and 7.5.
It is then possible in these both cases to adsorb cations or anions if the
pH of the solution is higher or lower than the I.E.P.S. of these two ampho-
teric gels.

3.1.2. Neutralization at constant pH

The second method which permits to follow the polarization of an oxide surface consists of measurements of oxides adsorption capacity at constant pH (2).

The procedure is as follows : an oxide is dipped into a aqueous solution, the pH of which is maintained constant by using ammonia or monochloracetic acid. The basic or acid quantities delivered to maintain pH at a given value are recorded as a function of time. These quantities corrected with the blank experiment, correspond to quantities neutralized by the support. It the support does not dissolve, they also correspond to the quantities of ions adsorbed on the support surface.

Fig.4 shows the amounts of ammonium or monochloracetate anions adsorbed on two supports of gamma alumina and silica as a function of pH. These results, obtained according to the method described above, lead to the same conclusions as with electrophoresis :

- Alumina by its amphoteric proporties, adsorbs ammonium cations and monochloroacetate anions at pH respectively higher and lower than 8. The particular point at pH 8 correlates well with the I.E.P.S. of gibbsite of figure 3 and with the several I.E.P.S. measurements of alumina in the literature (43).
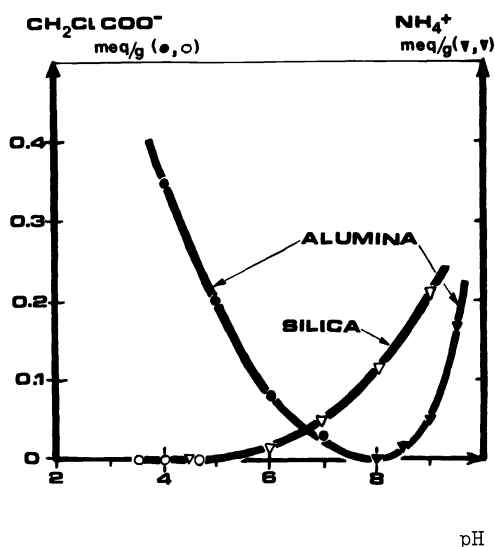- Silica adsorbs ammonium at pH higher than 6 but d'es not adsorb monochloracetate anions in the pH range studied.

Fig.4. Ammonium and monochloracetate adsorption on γ alumina or silica supports as a function of pH

(●,▼) : γ alumina of 190 m^2/g

(○,▽) : Silica of 160 m^2/g

(●,○) : 5 g of support + 100 ml of a 0.02 M solution of CH_2ClCOO Na ; addition of a 0.1 M solution of $CH_2ClCOOH$

(▼,▽) : 5 g of support + 100 ml of a 0.02 M solution of NH_4NO_3; addition of a 0.1 M solution of ammonia

In summary, a particle of oxide dipped in a solution at a pH lower than its I.E.P.S. tends to polarize positively and to adsorb compensating anions. On the contrary, the same particle dipped in a solution at a pH higher than the I.E.P.S. gets a negative charge on the surface which is compensated by adsorbed cations. Thus, three parameters seem to be important: the isoelectric point of the oxide, the pH at the impregnating solution and the charge of the ion to be adsorbed.

3.2. ANIONIC AND CATIONIC METALLIC COMPLEXES

Our practical aim is to prepare supported metallic catalysts by adsorp-

tion. We are now going to specify the form in which these metallic complexes
may occur.

    We can use two well-known families of complexes concerning a number of
metals from group 7a, 8 and 1b.

  - The family of chlorometallic complexes $(MCl_n)^{x-}$ shown in table 2.

TABLE 2
Anionic complexes of metals of 7a, 8 and 1b groups.

Mn MnO_4^-	Fe	Co	Ni	Cu
Tc	Ru	Rh $RhCl_6^{3-}$	Pd $PdCl_4^{2-}$	Ag
Re ReO_4^-	Os $OsCl_6^{2-}$	Ir $IrCl_6^{2-}$	Pt $PtCl_6^{2-}$	Au $AuCl_4^-$

    In this case, the metal is in the form of an anionic complex in which
the coordinating sphere is constitued by four or six chlorine atoms.

    We have, for instance, tetrachloraurate $(AuCl_4)^-$, hexachloroplatinate
$(Pt\ Cl_6)^{2-}$, hexachloroiridate $(IrCl_6)^{2-}$, tetrachloropalladate $(Pd\ Cl_4)^{2-}$,
hexachlorhodate $(Rh\ Cl_6)^{3-}$ and hexachloroosmate $(OsCl_6)^{2-}$ anions. To these
anions, we can add peroxide anions such as perrhenate $(ReO_4)^-$ and perman-
ganate $(MnO_4)^-$ anions in which the coordinating sphere is constituted by
four oxygen atoms instead of chlorine atoms.

  - The family of amine complexes $\underline{M}(NH_3)_n]^{x+}$ shown in table 3.

    In this family, the metal is in the form of a cation coordinated by se-
veral amine or ammonia groups.

    Among the most often used complexes, we can indicate the choropentamine
complexes of ruthenium, rhodium and iridium with valence III, the tetramine
complexes of palladium and platinum with valence II and amine complexes of
silver, copper, nickel and cobalt.

3.3. EXEMPLES

    To illustrate what we have said, we can now examine on the basis of re-
corded results in the literature, what the possibilities of adsorption
between several platinum complexes and silica or alumina are.

    For silica, two conditions are required : a solution pH higher than one
and preferentially about six and the use of a metallic cationic precursor.

TABLE 3

Cationic complexes of metals of 8 and 1b groups

Mn	Fe	Co $Co(NH_3)_x^{2+}$	Ni $Ni(NH_3)_x^{2+}$	Cu $Cu(NH_3)_x^{2+}$
Tc	Ru $Ru(NH_3)_5Cl^{2+}$	Rh $Rh(NH_3)_5Cl^{2+}$	Pd $Pd(NH_3)_4^{2+}$	Ag $Ag(NH_3)_x^{2+}$
Re	Os	Ir $Ir(NH_3)_5Cl^{2+}$	Pt $Pt(NH_3)_4^{2+}$	Au

These two conditions are not required with a chloroplatinic acid solution; this explains why chloroplatinic acid does not absorb on silica (2,4,6). With a tetramine platinum II chloride solution, we have a cationic complex but the pH of the solution is not high enough. Thus, the adsorption is very small (2,4). With a tetramine platinum hydroxide, both conditions are required and we have effectively in this case platinum adsorption(2,4). Likewise, utilisation of a solution which contains tetramine platinum chloride and ammonia leads leads to platinum adsorption (1,2,4,6).

For alumina, two conditions are also required : either an anionic precursor solution with a pH lower than about 8, or a cationic precursor solution with a pH higher than about 8.

In the cases of chloroplatinic acid solution, tetramine platinum hydroxide solution or tetramine platinum chloride ammonia solution, both conditions are required and in this way one obtains platinum adsorption (1,2,4,7-10,13). On the other hand, if we impregnate alumina with a sodium chloroplatinate solution, we have only very little adsorption because the solution pH is too near the isoelectric point of alumina. As to the tetramine platinum chloride solution, it does not lead to cation adsorption because the pH condition is not required.

Thus, the results actually published in the literature about platinum complex adsorption on oxides such as alumina and silica are consistent with the simplified schema presented before. We think that this schema remains valid for other oxides and other metallic complexes (3,5,11-13).
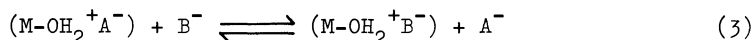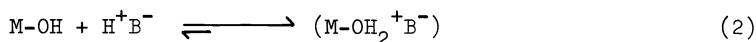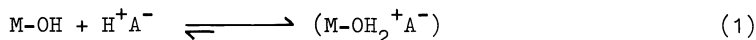
3.4. EXCHANGE OF ADSORBED SPECIES

Till now, we took the case of an oxide particle in contact with a solution containing one salt. Now, we are going to consider the case when the

impregnating solution contains, for instance, two mineral acids HA an HB.

If the oxide is basic or amphoteric, its surface polarizes positively and is surrounded by two types of counterions : A⁻ and B⁻.

Schematically, the three following reactions take place at the interface oxide-solution :

$$M-OH + H^+A^- \;\rightleftharpoons\; (M-OH_2^+A^-) \qquad\qquad (1)$$

$$M-OH + H^+B^- \;\rightleftharpoons\; (M-OH_2^+B^-) \qquad\qquad (2)$$

$$(M-OH_2^+A^-) + B^- \;\rightleftharpoons\; (M-OH_2^+B^-) + A^- \qquad (3)$$

The first and the second reactions correspond to the polarization of a surface site S-OH by HA or HB.

There are equilibriums displaced towards the right side. On the contrary, reaction (3) corresponds to a true exchange of A⁻ and B⁻ between oxide surface and solution.

To illustrate these various consideration, we can take the practical example of alumina impregnation by a hydrochloric acid and chloroplatinic acid solution.

According to (3) the equilibrium of exchange can be written as follows :

$$2(Cl)_{ads} + PtCl_6^{2-} \;\rightleftharpoons\; (PtCl_6)_{ads} + 2Cl^-$$
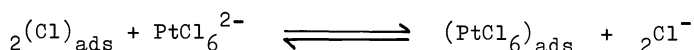
If the solution is diluted and assuming homogeneity of the alumina adsorption sites, we can express the equilibrium constant as follows :

$$K = \left[\frac{Cl^-}{Cl_{ads}}\right]^2 \cdot \frac{1}{Kd}$$

where Kd is the distribution coefficient of platinum between the solution and alumina.

Now, if we take the logarithm expression of the equilibrium constant, we should obtain a linear relation between $\log K$ and $[\log(Cl^-) - \log Cl_{ads}]$, in addition to a value for the slope equal to the valence of the metallic anion.

This is what we observe experimentally, when we impregnate gamma alumina with a hydrochloric solution of chloroplatinic acid, chloroiridic acid or chlorauric acid(figure 5). In the range studied, straight lines are obtained with slopes equal to about 2 for platinum and iridium and about 1 for gold.

Similar results are obtained when we impregnate silica with an ammonium buffer solution of platinum tetramine chloride, palladium tetramine chloride or amine copper salts (figure 6)

From a practical point of view, the reversibility of adsorption is very important because it permits to obtain a redistribution of the adsorbed complex ions on the polarized sites with a competive ion and thus, to obtain a homogeneous deposit of the metallic ion on the support.

3.5. ISOELECTRIC POINT OF OXIDES

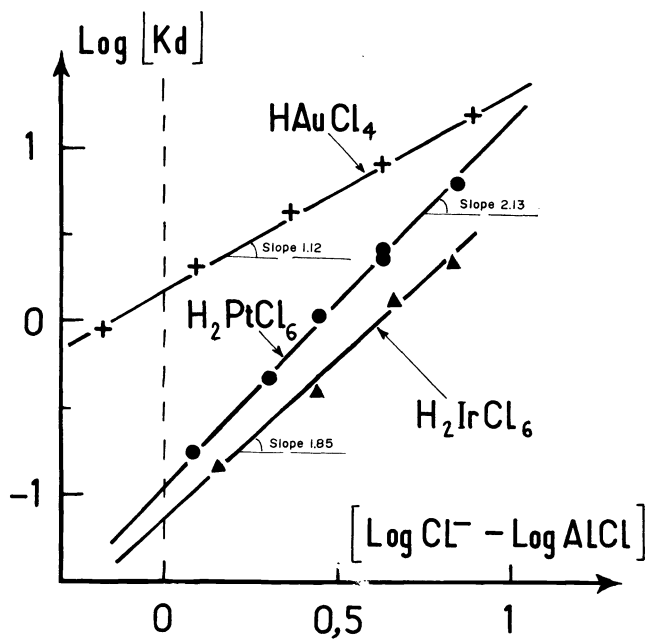We have seen that, given the isoelectric point of an oxide, we may es-

Fig. 5. Anionic exchange equilibrium - For details, see Ref. (13)
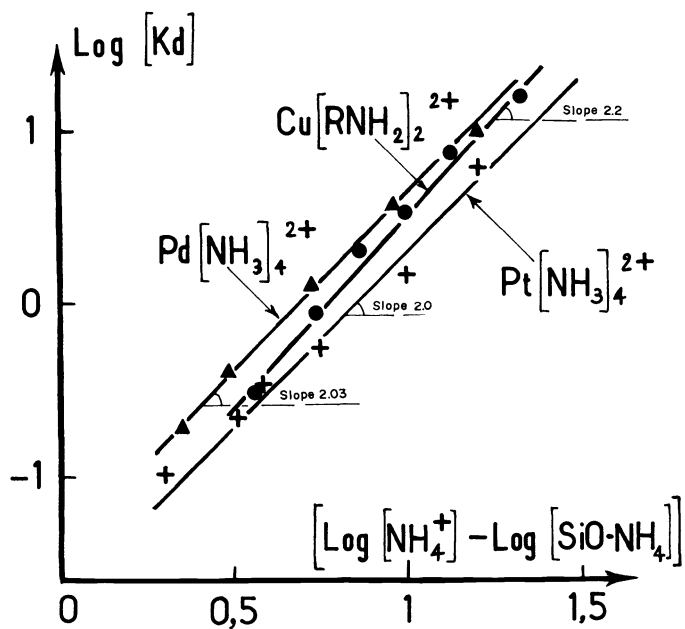

Fig. 6. Cationic exchange equilibrium - For details, see Ref. (13)

timate in advance the adsorption capability   (anionic or cationic) of this oxide and roughly what the pH range (acidic or basic) of the impregnating solution will be.

   Now, the isoelectric points of a large number of oxides and hydroxides are known and available in the literature. For this purpose, we can refer to the synthesis published in 1965 by PARKS (43).

   A number of values are given in table 4. They permit us to rank approximately the oxides in three categories :

   - The first one corresponds to the oxides that are acidic, such as Sb_2O_3, WO_3 or SiO_2. Their I.E.P.S. are very low and we may suppose that they are only able to serve as metallic complex cation adsorbants or exchangers.
   - The second one corresponds to the oxides that are basic, such as La_2O_3 or MgO. Their I.E.P.S. are very high, generally superior to 10. We think that these oxides are able to adsorb essentially metallic complex.
   - Finally, the third and most numerous one, include the oxides that are amphoteric such as TiO_2, Cr_2O_3 or Al_2O_3.

TABLE 4
Isoelectric points of various oxides.

Oxide	I.E.P.S.	Adsorption
Sb_2O_5	<0.4	
WO_3 Hydrous	<0.5	CATIONS
SiO_2 Hydrous	1.0-2.0	
U_3O_8	~4	
MnO_2	3.9-4.5	
SnO_2	~5.5	CATIONS
TiO_2 Rutile Anatase	~6	
UO_2	5.7-6.7	or
γFe_2O_3	6.5-6.9	
ZrO_2 Hydrous	~6.7	ANIONS
CeO_2 Hydrous	~6.75	
Cr_2O_3 Hydrous	6.5-7.5	
$\alpha, \gamma Al_2O_3$	7.0-9.0	
Y_2O_3 Hydrous	~8.9	
αFe_2O_3	8.4-9.0	
ZnO	8.7-9.7	ANIONS
La_2O_3 Hydrous	~10.4	
MgO	12.1-12.7	

Thus, with these values, we can hope approximately predict the behaviour of an oxide when it is impregnated by a solution of a metallic complex salt.

3.6. LIMITS AND SECONDARY PHENOMENA

In pratice, the preparation of metallic catalysts by complex adsorption may be limited or complicated by many factors or secondary phenomena. We describe below three of them.

3.6.1. Texture of the oxide

We have seen that an important adsorption capacity requires the choice of adequate pH conditions. However, this condition is necessary, but not sufficient in itself. Thus, if the oxide in operation has a low surface area, that is to say, a small number of adsorption sites, its adsorption capacity will be necessarily low.

For instance, we cannot hope to fix more than 0.2 wt % of platinum on an alpha alumina of 10 m^2/g from a chloroplatinic acid solution. In the same conditions, a gamma alumina of 200 m^2/g fixes about 3 wt % of platinum.

3.6.2. Stability of metallic complexes

The formulas of several chlorometallic and amine complexes have been listed in table 2 and table 3 to illustrate the possibilites of metallic anion and cation adsorption.

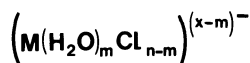The stability of these complexes is not always excellent.

For instance, in an aqueous medium, some chlorometallic anions are subject to aquation, hydrolysis, reduction (if the metal has several valences), and even polymerization reaction (45).

These reactions lead to different complexes whose formulas are given in table 5.
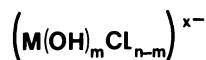
TABLE 5

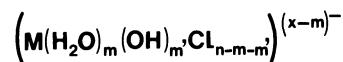Aquation, hydrolysis, reduction and polymerization of chlorometallic anions $(MCl_n)^{x-}$
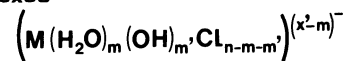
• **Chloro Aquo Complexes**

$$\left(M(H_2O)_m Cl_{n-m}\right)^{(x-m)^-}$$
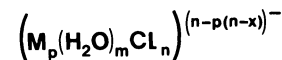
• **Chlorohydroxy Complexes**

$$\left(M(OH)_m Cl_{n-m}\right)^{x-}$$

• **Chloro Aquohydroxy Complexes**

$$\left(M(H_2O)_m (OH)_{m'} Cl_{n-m-m'}\right)^{(x-m)^-}$$

• **Reduced Chloro Aquohydroxy Complexes**

$$\left(M(H_2O)_m (OH)_{m'} Cl_{n-m-m'}\right)^{(x'-m)^-}$$

• **Polymeric Species**

$$\left(M_p (H_2O)_m Cl_n\right)^{(n-p(n-x))^-}$$

The kinetics of these reactions depends on a number of parameters such as pH, chlorine concentration or temperature.

Concerning the adsorption of these anions on oxides, the reactions of aquation, hydrolysis, reduction and polymerization modify the charge of the coordination sphere of the anion, and this modification may have a significant influence on the thermodynamics of the adsorption equilibriums.

In this case, there are as many exchange equilibriums as there are species in solution.

It is therefore important to know the metallic species in operation during impregnation, and, if possible, to maintain conditions where only one metallic species exists.

3.6.3. Solubility of the oxide

Apparent solubility of mineral oxides or hydroxides depends on their acid-basic character (figure 7).

For instance, solubility of an acid oxide or hydroxyde such as silica increases very rapidly in a basic medium. On the other hand, a basic oxide or hydroxide dissolves better in acid medium. As for amphoteric oxide, solubility increases as well for acid pH as for basic pH.

Anionic or cationic exchanges on basic or acid oxides often imply using solutions that are respectively acid or basic. Consequently, the support may dissolve if apparent solubility is high at the pH of the impregnation solution. In this case, it involves solubilization of ions containing the specific metal of the support.

This phenomenon of dissolution has been referred to many times in the literature for an alumina support that has been brought into contact with a solution containing a strong acid such as HCl or $H_2Pt Cl_6$ (8, 9, 10, 15, 46).

Figure 8 shows for example that when gamma alumina is in contact with a hydrochloric acid solution containing much more chlorine than that which corresponds to the adsorption capacity of the support, then, a part of the hydrochloric acid is adsorbed on the alumina, and the excess HCl is neutralized by surface dissolution of alumina into aluminium chloride (13).

4. CONCLUSIONS

By analyzing the phenomena that take place when an oxide particle is put into an aqueous solution, it is possible to bring out the importance of a specific property of the oxide : its isoelectric point (I.E.P.S) or zero point of charge (Z.P.C.).

In effect, an oxide in contact with a solution whose pH is below its I.E.P.S. tends to polarize positively and to be surrounded by compensating anions. On the other hand, the same oxide in a solution with a pH above its I.E.P.S. tends to polarize negatively and to be surrounded by compensating cations.
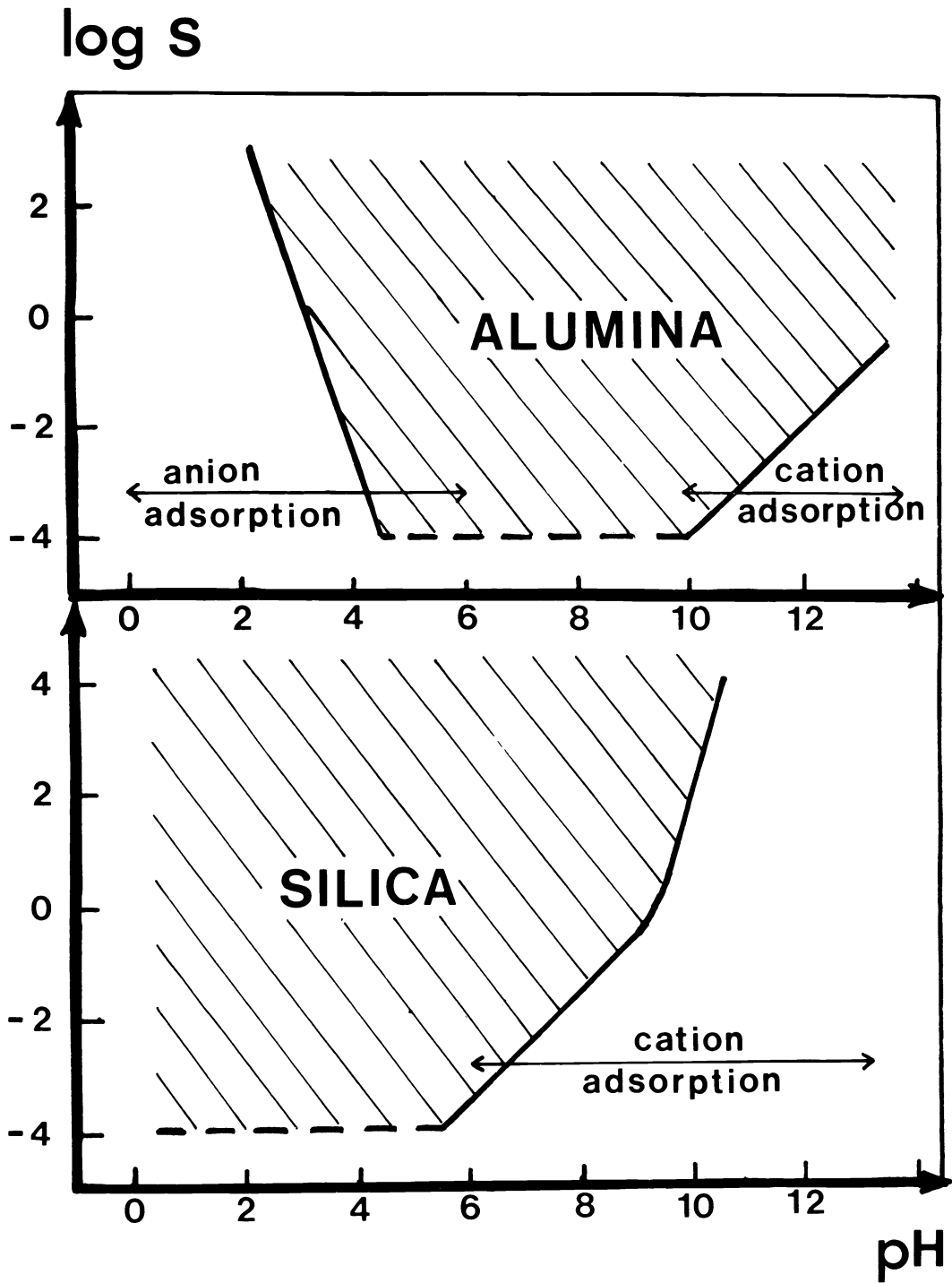
Fig. 7. Variation of the solubility of alumina and silica versus pH.
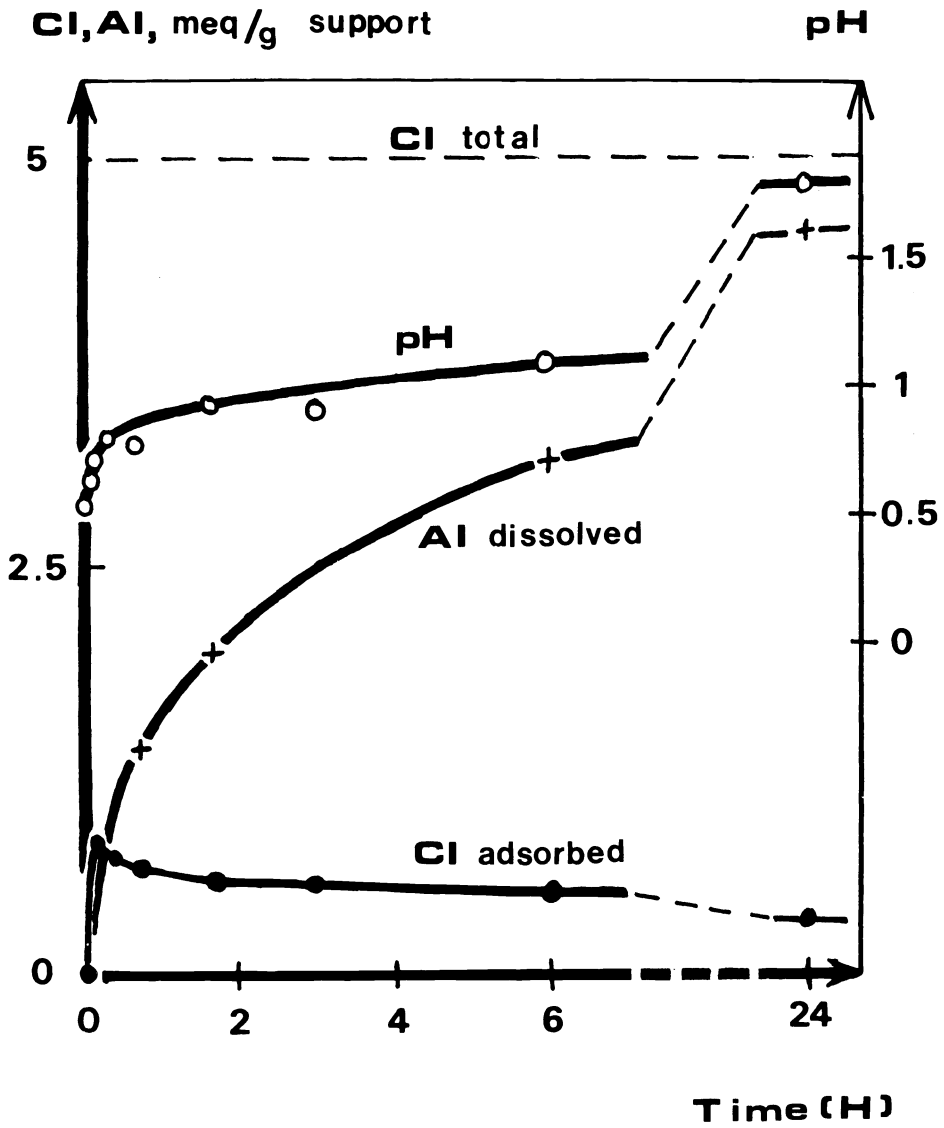
Fig.8. Chlorine adsorption and aluminium dissolution for the HCl-γ Al$_2$O$_3$ system.

With this simplified schema, the pH range that has to be used and the kind of metallic complexes (anions or cations) that must be selected can be estimated. Thus, the I.E.P.S. of an oxide and the pH of the impregnating solution seem to be the most important parameters that regulate adsorption of metallic complexes. However, knowing only the I.E.P.S. of an oxide is not enough. It must be kept in mind, for instance, that the capacity of cationic adsorption of silica becomes significant above pH 6, which is five pH units from its isoelectric point.

Consequently, in order to precisely know the adsorption capacity of an oxide at a given pH, it is preferable to know the evolution of the polarization as a function of pH. This can be done, for example, either by measuring electrophoretic velocity, or by neutralization experiments at constant pH.

Not withstanding the complication raised by secondary parameters such as small surface area of the oxide, instability of the metallic complexes or solubilization of the oxide, we think that all these considerations which seem to be valid in the case of metallic complex adsorption on alumina or silica, are also valid for other oxides.

Furthermore, other possibilities may be envisaged, such as the doping of a catalytic active oxide by surface adsorption of a foreign metallic ion, or even the selective depositing of a metal on one of the constituents of an oxide mixture. This is to be confirmed, however, through further original experiments.

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