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Catalyst Impregnation: Reactions of Noble Metal Complexes with Alumina[1]

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The rates of uptake of noble metal complexes over the surfaces of porous alumina are controlled partially by pore diffusion and partially by the rate of the chemical process between the metal complex and the alumina, resulting in impregnation profiles of different shapes. The rate of removal of metal complexes by alumina from solution is inversely related to the depth to which the noble metal penetrates into the alumina pellet. For those complexes that are rapidly removed from solution, the noble metal profile resembles a sharp shallow band, located at the pellet's outer edge. On the other hand, for those complexes that are slowly removed from solution, the noble metal profiles in the pellets are essentially uniform along the radius of the catalyst pellets. Anionic chloride complexes, e.g., MCl_6^{n-} and MCl_4^{n-}, appear to react with alumina surfaces by a ligand displacement reaction. For a series of $(NH_4)_aMCl_6$ complexes, the relative reactivities toward γ-alumina are Pd > Rh > Ru $\gg$ Pt $\simeq$ Ir.

INTRODUCTION

Automobile exhaust emission control catalysts in current use contain both platinum and palladium supported on alumina. When chloride solutions of Pt and Pd are impregnated onto an alumina support, electron microprobe studies reveal that Pt and Pd differ in their distribution on the alumina: Pd tends to be located in a shallow layer near the surface of the catalyst pellets, while Pt penetrates considerably deeper into the pellet's interior (*1*). This observation suggests that the two noble metals may interact differently with the alumina during the impregnation process.

This study was undertaken to determine the important parameters controlling noble metal penetrations and the means by which they can be manipulated during the impregnation process.

Simple diffusion–reaction processes can be conveniently analyzed in terms of the Thiele parameter, h [e.g., Ref. (2)]:

$$h = R\left(\frac{k\ a\ C_O{}^{n-1}}{D}\right)^{\frac{1}{2}}.$$

Applied to the catalyst impregnation problem the variables are the following: R (centimeters) is the pellet radius, k is the intrinsic rate of the surface reaction, a (square centimeters per cubic centimeter of pellet) is the specific surface area of the support, C_O is the concentration of impregnant in the bulk solution (moles per cubic centimeter), n is the kinetic order of the reaction of impregnant with the support surface, and D (square centimeters per second) is the effective diffusivity of the noble

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metal complex in solution into the pores of a catalyst pellet.

The derivation and detailed implications of the Thiele parameter will not be described here. Its use has been well explored in the literature (*2*), and its utility in catalyst impregnation studies has also been discussed (*3*). It is perhaps enough to say that the Thiele parameter expresses the ratio of the reactivity of a species to its diffusivity. Consequently, a large h value means a fast reaction with the support and/or slow diffusivity and, hence, a steep concentration profile in the catalyst pellet (i.e., shallow penetration depth). Conversely, a small h value means that the diffusivity of the species is faster than its reactivity with the support, resulting in flat (and deep) concentration profiles in the catalyst.

According to these considerations, the impregnation properties of a given catalyst can be influenced by either changing the intrinsic reaction rate (k) of the noble metal complex with the support surface (i.e., by varying the nature of this metal complex or the nature of the surface), by changing the specific surface area (a), or by changing the diffusivity (using a smaller or larger metal complex or using a support with smaller or larger pores in which the diffusion occurs).

Of these possibilities, this paper explores only the manipulation of k, the intrinsic rate constant. This will be accomplished by varying the complex of a given noble metal or by varying the noble metal associated with a given ligand.

EXPERIMENTAL

The noble metal complexes used in this study were purchased from either Alfa Products or Research Organic/Inorganic Chemical Corp. and were used as received. The $NH_4[Pt(C_2H_4)Cl_3]$ was prepared according to the method of Chatt and Duncanson (*4*) except that $(NH_4)_2PtCl_4$ was substituted for K_2PtCl_4. The purity of the product was verified by elemental analysis and ir spectroscopy.

The reaction of noble metal complexes with alumina was studied by mixing 50 cm^3 of γ-alumina spheres (BET surface area: 75 m^2/g) with 100 cm^3 of an aqueous solution containing the noble metal complex. In all experiments, the initial noble metal concentration were kept at 4.56×10^{-3} *M*. The alumina and noble metal solutions were placed in a 250-cm^3 beaker at room temperature. The pellets were stirred by a magnetic stirrer for 1, 5, 10, 30, and 60 min. At the end of each time interval the solutions were decanted, filtered, and analyzed for noble metal content. In some experiments the free or uncoordinated ligand content of the solution was also determined. These measurements were performed by using a pH meter equipped with either a Cl^-- or a NH_4^+-specific ion electrode. After the impregnation process, the catalyst pellets were washed with two or three portions of 100 cm^3 of distilled water and air dried, at room temperature. The Pt and Pd penetrations were determined by the $SnCl_2$ staining technique (*5*). An analogous method was developed to measure Rh penetrations: the pellets were boiled for 3 min in an aqueous 2 *M* NaOH solution containing sodium sulfide (0.1 g of Na_2S/cm^3 of solution). After this treatment, a darkened band indicated the location of Rh in these pellets.

RESULTS AND DISCUSSION

Mechanisms of Adsorption

The reaction of noble metal complex ions with alumina surfaces is governed by both diffusion and kinetic or reactivity considerations. Our findings suggest there are two distinct mechanisms.

One type of mechanism involves the reaction of the noble metal species with a surface site which results in the displacement of a ligand from the metal's coordination sphere:

$$ML_a^{n-} + [\text{O-Al}] \rightarrow [ML_{a-1}\ldots\text{O-Al}]^{n-} + L.$$

Evidence for this type of mechanism comes from the observation of increasing quantities of free ligand in solution concomitant with the rapid uptake of certain noble metal complexes. It is also known that $PdCl_2$ reacts with Al_2O_3 to give a species whose electronic adsorption spectrum is significantly different from that of $PdCl_2$ (*6*).

The uptake of several chloro complexes of Pt and Pd was studied at different time intervals. The noble metal uptake and the uncoordinated free chloride ion content of the reacting solutions were simultaneously determined. The rapid removal of the Pd complexes $PdCl_4^{2-}$ and $PdCl_6^{2-}$ from solution (Fig. 1) was accompanied by a rapidly increasing free chloride ion content in the liquid. The Pt complexes, although only slowly removed from solution (Fig. 1), released significant quantities of chloride ions after 60 min of reaction (Table 1). The ratios of the quantity of metal ions adsorbed to the quantity of Cl^- ions released into solution for the Pd complexes is about 1. For the Pt complexes it is about 2. The appearance of Cl^- ions in solution is supportive of a ligand displacement reaction occurring between the Pt and Pd complexes and the support. While it is tempting to try to relate

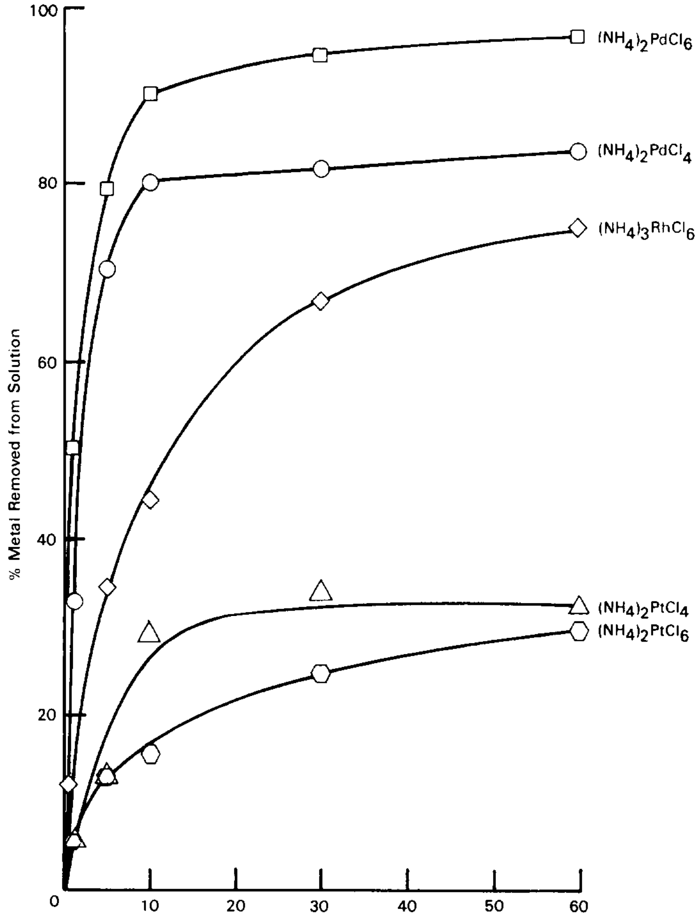


FIG. 1. Uptake of various noble metal chloride complexes by Al_2O_3 from solution.

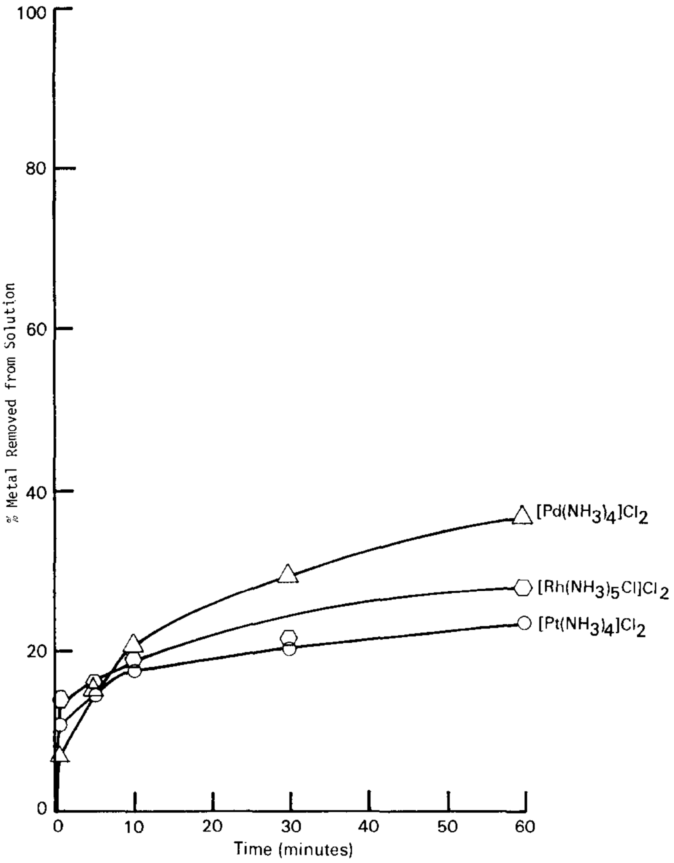


FIG. 2. Uptake of various noble metal ammonia complexes by Al_2O_3 from solution.

these ratios to the quantities of complex reacting with the Al_2O_3 and the quantities of complex trapped in the pore structure, we did not attempt to do this since Cl^- ions are known to react with Al_2O_3 (*7*), and we cannot be sure that the Cl^- ion content measured, therefore, represents the total quantity released into solution.

Noble metal ammonia complexes may react with alumina surfaces by an ion-exchange process (*8*). Complexes of the type $[M(NH_3)_4]^{2+}$ and $[M(NH_3)_5Cl]^{2+}$ exchange onto alumina by reacting with some surface site. Ligand displacement does not appear to occur: No uncoordinated NH_3 was found in solution after the experiments. As shown in Fig. 2, the ammonia eomplexes tend to be removed slowly from solution.

For the less reactive complexes, the possibility exists that some of the complex crystallizes in the pores without reacting with the surface.

Reactivity and Penetration Depth

The rate of removal of metal complexes from solution by alumina is inversely related to the depth to which the noble metal penetrates into the alumina pellet. For those complexes that are rapidly removed from solution, e.g., H_2PtBr_6, $(NH_4)_2PdCl_4$, and $(NH_4)_4RuCl_6$, the noble metal profile resembles a sharp shallow band, located at the pellet's outer edge. After 60 min, the noble metal penetrated only about 200 μm into the pellet (Table 2).

On the other hand, for those complexes that are slowly removed from solution, e.g.,

TABLE 1

Appearance of Uncoordinated Chloride Ions in Solution

	Metal adsorbed after 60 min (μmol/cm^3)	Uncoordinated Cl^- ions generated after 60 min (μmol/cm^3)	Adsorbed metal (Cl^- ions released)
$(NH_4)_2PdCl_4$	3.83	4.48	0.86
$(NH_4)_2PdCl_6$	4.41	4.34	1.02
$(NH_4)_2PtCl_4$	1.48	0.70	2.11
$(NH_4)_2PtCl_6$	1.35	0.59	2.29

$NH_4[Pt(C_2H_4)Cl_3]$, $K_2Pt(SCN)_2$, $(NH_4)_2IrCl_6$ the noble metal profiles in the pellets are essentially uniform along the radius of the catalyst pellets. These complexes penetrated the entire alumina pellet after only 1 min or less.

For the more reactive complexes, the noble metal species penetrated only 100–150 μm during the first minute of reaction. Figure 3 shows the relationship of reaction time and metal penetration depth for the relatively reactive H_2PtBr_6. After 1 min, 39.6% of the H_2PtBr_6 was removed from solution. It had penetrated 143 ± 14 μm. After 5 min, 69.6% of the complex was removed, but the penetration depth increased only ~26 μm to 160 ± 25 μm. At 60 min essentially all (96.7%) of the H_2PtBr_6 had been adsorbed, and the penetration depth reached 224 ± 16 μm.

In the above impregnation experiments dry alumina was added to aqueous solutions which contained the noble metal complexes. Therefore, the possibility existed that the penetration properties of the complexes might be strongly influenced by the initial rapid uptake of solution by the dry alumina. An experiment was performed to assess the effect of the relative dryness of the alumina on the reaction–diffusion properties of $(NH_4)_2PdCl_4$. Dry alumina and alumina which was presoaked overnight in distilled water were exposed to aqueous solutions of $(NH_4)_2PdCl_4$. The wet alumina was taken directly from its water bath with no attempt being made to dry it. Although the penetration depths obtained from the presoaked alumina were slightly more shallow than those obtained from the dry alumina, the differences were small and not statistically significant at a 5% confidence level. Thus, the relative dryness of the alumina appears to play only a minor role in influencing the results of our experiments.

Reactivity Differences Between Metal Complexes

In order to understand why Pd complexes, for example, are more reactive toward alumina than their Pt analogs, it is necessary to consider the mechanisms by

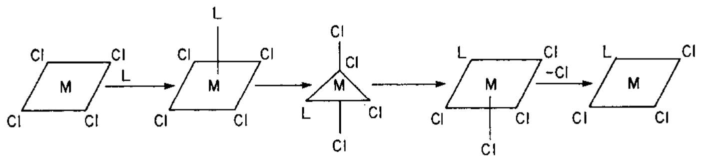
TABLE 2

Reactivity and Penetration Depth of the Complexes

Complex	Metal absorbed after 60 min (%)	Metal penetration[a] (μm)
High reactivity		
H_2PtBr_6	96.7	224 ± 16
$(NH_4)_2PdCl_4$	83.9	205 ± 46
$(NH_4)_2PdCl_6$	96.7	227 ± 35
$(NH_4)_3RhCl_6$	75.0	198 ± 39
NH_4AuCl_4	97.0	—
$(NH_4)_4RuCl_6$	63.8	—
Low reactivity		
$(NH_4)_2PtCl_4$	32.4	Uniform
$NH_4[Pt(C_2H_4)Cl_3]$	20.0	Uniform
$(NH_4)_2Pt(NO_2)_4$	45.5	Uniform
$(NH_4)_2PtCl_6$	29.6	Uniform
H_2PtCl_6	33.4	Uniform
$K_2Pt(CN)_4$	22.9	Uniform
$K_2Pt(SCN)_4$	22.5	Uniform
$[Pt(NH_3)_4]Cl_2$	23.2	Uniform
$[Pd(NH_3)_4]Cl_2$	36.4	Uniform
$[Rh(NH_3)_5Cl]Cl_2$	27.0	Uniform
$(NH_4)_2IrCl_6$	28.8	Uniform

[a] Values given are the average ± SD for ten pellets, determined by $SnCl_2$ or $Na_2S/NaOH$ staining.

which they undergo ligand displacement reactions. Let's first consider square planar complexes such as the chlorides, $PdCl_4^{2-}$ and $PtCl_4^{2-}$. The mechanism of ligand displacement has been the subject of intensive investigation (*9, 10*) and the reaction pathway is generally acknowledged as follows (*10*).



The rate-determining step for ligand displacement reactions of square planar d^8 complexes, e.g., Pt(II) and Pd(II), appears to be the first step of this reaction sequence (*11, 12*). The attack of the incoming ligand (L) most likely occurs at the empty P_z orbital localized on the central metal ion. The initial hybridization of the metal ion is dsp^2. Hence the transition state involves a rehybridization of the metal orbitals to dsp^3 (*10, 11*). The energy required for rehybridization is a sensitive function of the metal ion and varies considerably from metal to metal. For a series of complexes having different central metal ions but otherwise being of the same geometry, the reaction rates for ligand substitution will tend to vary significantly. For example, for the reaction of pyridine with a series of $[MCl(o\text{-tolyl})\text{-}(PEt_3)_2]$ complexes, where M = Ni, Pd, and Pt, the reaction rates are $5 \times 10^6 : 10^5 : 1$, respectively (*13*). Similar results have been obtained for a series of $[Pt(dien)X]^+$ and $[Pd(dien)X]^+$ complexes where X = Cl^-, Br^-, I^-, SCN^-, and NO_2^- (*14*). These relative ligand substitution rates seem to be in accord with the rate in which these d^8 metal ions expand their coordination number (*10*).

In our desire to study the reactions of square planar Pt complexes with alumina, we attempted to vary the reactivity of the

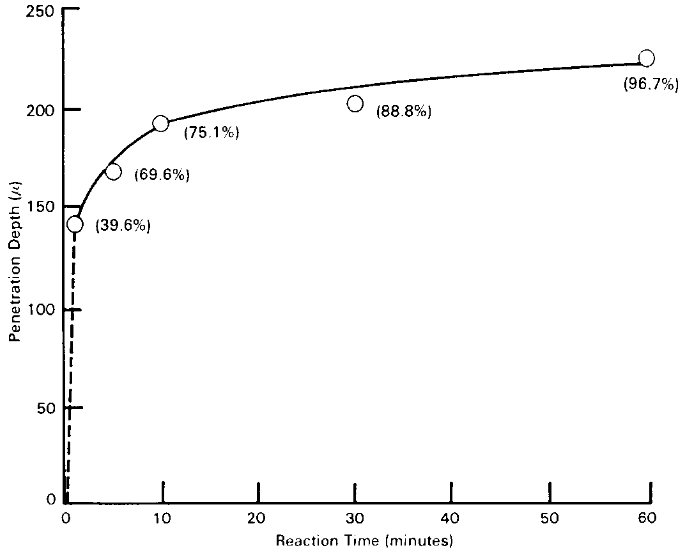
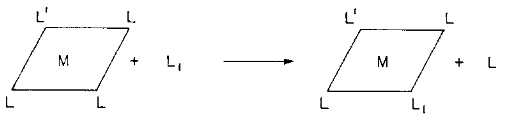


FIG. 3. Effect of reaction time on Pt penetration depth for H_2PtBr_6. Numbers in parentheses refer to the percentage of H_2PtBr_6 removed from solution.

complex by manipulating the ligand field geometry of the central Pt ion. This was done in order to utilize the well-known "*trans* elimination effect" (*15*). When square planar complexes of the type $[M(L)_3(L')]$ (where L′ may be L) react with a ligand (L_1), the quantity of product formed is a function of the nature of L′ (*15*). An extensive series of ligands may be placed in sequence of their ability to direct *trans* substitution (*15*).



In the approximate order of their ability to direct *trans* substitution, the sequence is as follows: CN^-, $C_2H_4 > NO_2^- > SCN^- > Br^- > Cl^- > NH_3$, H_2O, OH^- (*15*). In our experiments it was hoped that, by judiciously selecting ligands of different *trans* directing strengths, it would be possible to control the Pt penetration depth into the catalyst pellets by proper choice of a square planar Pt complex. As Table 2 indicates, none of the square planar complexes studied were sufficiently reactive with the alumina to allow this degree of control.

The octahedral Pt(IV) complexes were found to exhibit a wider range of reactivities with Al_2O_3 than the square planar Pt(II) complexes. The differences in reactivity can again be rationalized by considering the mechanisms of ligand displacement reactions of octahedral complexes. The reaction involves a two-step process (*9, 11*):

$$ML_6 \rightarrow ML_5 + L,$$
$$ML_5 + L_1 \rightarrow ML_5L_1.$$

In the first step a M–L bond undergoes dissociation. Hence the metal–ligand bond strength is a important determinant of the relative ease of ligand displacement. The relative order of bond strengths of transition metal complexes can readily be predicted from the spectrochemical series (*15*). For a series of common ligands the order of increasing metal to ligand bond strength is $CN^- > NO_2^- > NH_3 > H_2O > OH^- > Cl^- > Br^- > I^-$.

We investigated the reactions of the three octahedral halide complexes, PtI_6^{2-}, $PtBr_6^{2-}$, and $PtCl_6^{2-}$, with alumina in an attempt to find Pt complexes that exhibit a wide range of reactivities. The PtI_6^{2-} ion decomposed upon contact with the alumina, releasing I_2. This complex was not studied further. As seen previously, the $PtCl_6^{2-}$ ion was not very reactive with alumina (Fig. 1). The $PtBr_6^{2-}$ ion, on the other hand, was quite reactive (Table 2 and Fig. 3).

It appears that the Pt–Br bond is sufficiently weak to permit a rapid dissociation and subsequent reaction with the available surface sites on alumina. By contrast, the Pt–Cl bond is stronger and undergoes dissociation and subsequent reaction with the alumina surface sites more slowly.

ACKNOWLEDGMENTS

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