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THE EFFECT OF CATALYST PREPARATION ON CATALYTIC ACTIVITY

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The Effect of Catalyst Preparation on Catalytic Activity

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Abstract

Three intrinsically connected phenomena occur during adsorption/impregnation of aqueous electrolytes onto oxide carriers. They are: pH-dependent development of surface charge carriers on the oxide; pH-dependent aqueous speciation of catalytic precursors; surface adsorption by complexation and coordination. Modeling of these processes yields basic thermodynamic properties of the adsorbed phase, which could provide useful information of the catalytic properties of the metal, support, and reveal metal-support interactions, thus contributing to design criteria for supported-metal catalysts.

The spectrum of catalytic systems that can be studied using the above approach is greatly extended when both pure and composite oxide carriers are considered. This presentation will focus on three metal/support systems, each of which provides results of both practical and fundamental importance.

1. INTRODUCTION

During the preparation of supported metal catalysts, the adsorption of aqueous metal ions is influenced by the intrinsic properties of the support. Any attempt to model this adsorption phenomenon requires at least three elements: the pH-dependent surface charge speciation of the support, the pH-dependent aqueous phase speciation of the precursor ion, and a suitable model to describe the equilibrium exchange reaction.

1.2 pH-Dependent Surface Charge

The surface chemistry of an oxide surface in contact with an aqueous solution is determined to a large extent by the protonation/deprotonation of their hydroxyl groups. The equilibria may conveniently be expressed as [1]:

By appropriate adjustment of pH, the surface may carry a net positive or negative charge. At a specific pH, the surface has zero charge. This point of zero charge (PZC)

more correctly defines the situation where there is a net zero charge on the surface; it is readily determined by either mass titration or potentiometric titration methods [2,3]. The pH at the PZC has a specific value for each oxide which depends on the electronic character of the metal-oxygen bond and the stoichiometry of the surface.

The point of zero charge, where $[\text{MOH}_2^+] = [\text{MO}^-]$, is related to the two intrinsic acidity constants by the following equation [4]:

$$\text{PZC} = \frac{(\text{p}K_1 + \text{p}K_2)}{2} \quad (2)$$

The fraction of charged sites at the PZC is related to the difference in the two pK values (i.e., $\text{p}K_2 - \text{p}K_1$) [1,5]. The value of $\text{p}K_2 - \text{p}K_1$ is denoted as DPK. It has been demonstrated in the literature that the DPK is also an important parameter for determining the pH-dependent distribution of ionizable surface groups [1,6].

Numerous models have been proposed for describing the surface charge development of metal oxide surfaces. These include the constant capacitance model [4], the diffuse layer model [7], the Stern model [8], and the triple layer model [9]. Each representation is distinguished by the manner in which it depicts the electric double layer (edl). We have found that a simple diffuse layer model accurately predicts the adsorbed amounts of ionic solutes [3,10]. The diffuse layer model possesses simplicity in that all adsorption is assumed to occur in one surface layer, thus eliminating multiple planes for adsorption at the surface and the associated fitting parameters.

In our studies, DPK values are determined by graphical extrapolation combined with a numerical technique according to the procedures described by Noh and Schwarz [10]. This method does not assume that the presence of positive or negative sites can be ignored for the pH range where negative or positive sites, respectively, become dominant. Thus, data near the PZC can also be utilized in the extrapolation technique. To avoid any ambiguity in extrapolation of the data to the PZC, a least-square error regression is applied for a given set of data. Another advantage of the DPK determination by this method is that the value of N_s , the total number of ionizable sites, can also be estimated. The three parameters, PZC, DPK, and N_s are the requisite data base for evaluating the pH-dependent surface charge development of an oxide surface. This modeling procedure provides a semi-quantitative chemical signature of the acidic properties of each oxide. Furthermore, in an aqueous environment, the adsorption properties of each oxide can be estimated if equilibrium adsorption experiments are carried out at different pH values, and if the aqueous speciation of the catalytic precursor compound is known. We would expect that the saturation capacities for precursor adsorption would "track" the number of charge carriers provided adsorption was predominantly controlled by electrostatic interactions. It is important to note that precursor ions serve, in effect, as titers of the protonated and deprotonated hydroxyl groups under the prevailing experimental conditions. Thus, metal-support interactions can be "controlled" on a single support by simple variation of the preparation conditions. It is one aspect of our studies to determine what, if any, affect these metal-support interactions might have on catalyst performance.

1.3 Adsorption at Constant pH

Adsorption data at constant pH obey the Langmuir isotherm

$$\frac{q}{s} = \frac{KC}{(1 + KC)} \quad (3)$$

where q (moles/kg.cat) is the adsorbed amount at equilibrium, s is the saturation capacity, and C is the equilibrium concentration in solution (mols/lit). This simple equation is chosen because it well represents a broad spectrum of experimental adsorption isotherms. Other isotherms such as Henry, Freundlich, or Tempkin can be described by Equation (3) over a certain concentration range depending on the values of $KC_{\max}$ [11]. In addition, the parameters of the Langmuir isotherm, equilibrium constant K (lit/mol) and the adsorption capacity of the supports (moles/kg) have physical meaning in terms of adsorption-desorption equilibria. When adsorption is strong, K is large. Thus, experiments of this type can be used to assess the strength of metal-support interactions, and this can be done for either protonated or deprotonated hydroxyl groups.

The Langmuir constant, K , is an apparent equilibrium constant that includes a term for the electrostatic interaction energy. The intrinsic value of the Langmuir constant can be determined by extrapolation to the pH (PZC). This results in an expression where

$$\log K_{INT} = \log K + \frac{Ze\phi}{2.3kT} \quad (4)$$

Z is a stoichiometric coefficient and ϕ is the surface potential evaluated at the pH of the adsorption measurement. It can be shown that ϕ is linearly related to the difference $|pH - pH(PZC)|$ [9].

1.4 pH-Dependent Aqueous Speciation

The chemical speciation of a catalytic precursor ion is determined by the properties and concentration of the precursor salt, the solution pH and ionic strength, and the presence of added or extraneous counterions [5]. The term speciation refers to the actual form in which a molecule or ion is present in solution. In all solution environments, bare metal ions are in a continuous search for a partner. For example, all metal cations in water are hydrated, thus forming aquocomplexes. The coordination reactions in which metal cations participate in aqueous solutions are exchange reactions with the coordinated water molecules exchanged for some preferred ligands. The ligands could be counterions in solution as "sites" on an oxide surface.

Multivalent metal ions participate in a series of consecutive proton transfers. All hydrated ions can, in principle, donate a larger number of protons than that corresponding to their charge and can form anionic hydroxo-metal complexes. Because of the limited pH ranges of aqueous solutions, not all elements can exist as anionic hydroxo or oxo complexes.

In our studies, we find it most desirable to choose catalytic precursor salts whose chemical speciation is reasonably well documented. For example, dissolved $\text{Co}(\text{NO}_3)_2$ at concentrations equivalent to loading ≤ 10 wt-% of metal onto conventional supports and whose ionic strength does not exceed $\sim 1\text{M}$ will exist predominantly as equated Co^{2+} ($\text{Co}(\text{H}_2\text{O})_6$) $^{2+}$ for pH values less than ~ 7 [5]. The chemical state of palladium (II) ions in aqueous media containing chloride and/or ammonium ions depends on the pH and on other solution variables [12]. The palladium (II) ions form various complex species with

chloride and/or ammonium ligands, with electric charges between -2 to +2. Palladium (II) species are stable at pH values < 2 as PdCl_4^{2-} and for pH values > 8.0 as $\text{Pd}(\text{NH}_3)_4^{2+}$ species.

2. SURFACE ADSORPTION

One "quality" of hydroxyl groups on oxides is the role they serve as adsorption or exchange sites during catalyst preparation. There have been several studies of catalytic metal ion adsorption on different oxide supports. Coordination reaction between ionic complexes and surface hydroxyl groups have been shown to occur with some mono- and di-valent cations [9,13]. Brunelle [14] has proposed an adsorption model which emphasizes the electrostatic aspects of the adsorption process. Wang and Hall [15] have shown that such an electrostatic mechanism can be used to interpret the adsorption of several metal ions on different supports (i.e., TiO_2 , Al_2O_3 , SiO_2 , and MgO).

The adsorption behavior of hydrous alumina surfaces has been interpreted by the site-binding model [4,9,13,16,17]. This is a reasonably complete model, in which chemical and physical interactions are considered together in calculating surface-solution equilibria. This model has been used to characterize the adsorption-equilibria of hydrated metal cations and/or metal complex anions on various supports [4,9,13,16]. According to the site-binding model, the principal mechanism of transfer from the aqueous phase to the surface is the reaction of solute ions with ionizable surface sites [9]. To characterize the adsorption process for a series of oxides, a simplifying assumption is often made. It is that adsorption of ionic solutes is controlled only by surface charge. This is not true unless the ionic solute neither hydrolyzes to form hydroxo complexes in solution nor interacts with the surface through any non-electrostatic bond. These possibilities appear to depend upon the metal ion/oxide system studied and the experimental conditions. Each must be carefully considered in the design of experiments to demonstrate the impact of catalyst preparation on catalyst performance.

3. COMPOSITE OXIDES

A new class of materials can be obtained by modifying the surface of bulk oxides with attached clusters of other oxides [18-20]. Cluster compounds of metal oxides can be prepared by impregnation of supporting oxides with a precursor compound which generates a second phase oxide by suitable fixing procedures. When the second phase oxide wets the support, well-dispersed surface clusters can be formed which modify dramatically the interfacial properties of the bulk oxide [21,22]. This class of materials has been referred to as composite oxides. They differ from the binary oxides used presently as catalyst supports (the most common of them being silica-aluminas) by the important feature that the second component is well dispersed on the surface of the main oxide.

Composite oxides offer unique properties for supporting catalytic metals. Controlled regulation of the impregnation pH can result in a selective ion adsorption (or exchange) either on one or on both of the oxidic components. For example, since the PZC of silica and alumina are separated by at least 4-5 pH units, a "window" exists in the pH

range of 3 to 8 where silica is progressively more negatively charged while alumina still carries positive charges. Within this pH range, a composite oxide consisting of a low concentration of alumina clusters deposited over a silica surface could be capable of selective ion exchange of cations only with silica surface sites. Beyond the PZC of alumina (pH ~ 8-9), an increasing cationic exchange with alumina sites becomes possible, but adsorption on the more negatively charged silica surface should still prevail.

This design strategy depends on the idea that adsorption of ionic solutes is controlled by surface charge and that each phase of a composite oxide develops charge, as a function of pH, in the same manner as its bulk counterpart. Experimental results from our laboratory, as described below, indicate that such assumptions are valid.

4. ADSORPTION/IMPREGNATION OF Pd(II) COMPOUNDS ON ALUMINA

Hydroxyl inventories on typical oxide surfaces will vary with treatment temperature and the "quality" of the resulting inventory can be assessed by modeling the pH-dependent development of each oxide's surface charge. To demonstrate the validity of this assertion, this section presents results we have recently obtained.

4.1 Effect of Oxidation Temperature on Surface Charge Speciation

Portions of a laboratory-prepared Al_2O_3 were calcined (after drying) at 675K and 975K. Figure 1 was constructed to establish a basis for conducting Pd(II) adsorption experiments. The fractional surface charge, determined as explained in the Introduction, was converted into an absolute number of charge carriers using the N_s values obtained for each support. A portion of the pH-dependent surface charge development for the two alumina samples is shown in the low pH (Fig. 1a, positive charge dominated) and high pH (Fig. 1b, negative charge dominated) regions. There is a significant change in the number of positive/negative charge carriers which depends on the sample's calcination temperature.

Figure 1: Surface Charge Speciation as a function of pH on the alumina support calcined at 675K and 975K a) positive sites b) negative sites

4.2 Effect of pH on Pd (II) Adsorption

Figure 2 illustrates the effect of pH on $\text{Pd}(\text{NH}_3)_4^{2+}$ adsorption. The results show that $\text{Pd}(\text{NH}_3)_4^{2+}$ adsorption is proportional to the number of negative sites. As the pH is lowered, the number of negative sites decrease and there is a corresponding increase in the number of unionized sites. The apparent "enhanced" adsorption, which increases with decreasing pH, is ascribed to deviations from the site-binding model due to direct exchange with hydroxyl groups. The PZC of this alumina is 8.66. If adsorption is electrostatically controlled, at the PZC the surface attains a net zero charge. From Figure 2, it is clear that at pH ~ 8.66 , the palladium adsorption is zero.

Figure 2: Effect of pH on the adsorption of $\text{Pd}(\text{NH}_3)_4^{2+}$ and surface charge speciation on alumina support calcined at 975K $\square$ Pd (II) adsorption $\bullet$ Positive sites

5. DEMONSTRATION OF SELECTIVE METAL-SUPPORT EXCHANGE ONTO COMPOSITE OXIDES

We have found that it is extremely important to have a thorough knowledge of the support material before attempting to prepare supported metals. Such considerations as the compounds available to prepare the composite oxide series, the point of zero charge (PZC) of the pure oxides, their surface areas, and the effects of the second phase oxide on the BET surface area of the composite all enter into our understanding of the morphology of these materials. The next two sections briefly describe our results for two composite oxide/metal systems.

5.1 Co/WO₃/Al₂O₃

Composite oxides of WO/Al₂O₃ have been prepared, and their surface morphology and surface charge development in water have been determined. Cobalt has been supported on a 12% WO₃/Al₂O₃ composite. Temperature-programmed reduction, CO temperature-programmed reaction (TPRx), CO/H₂ methanation, ethane hydrogenolysis, and XPS results strongly suggest that the Co²⁺ cation is selectively exchanged onto the second phase, WO₃, of the composite. The activity measurements, furthermore, demonstrate the Co supported on the composite oxide has a significantly higher activity than Co supported on either of the pure phases.

5.2 Adsorption

Preliminary experiments were performed to determine the appropriate conditions for preparing the catalysts used in this study. Cobalt solutions with a concentration sufficient to mount 3% by weight of metal, assuming all the Co was transferred to the support, were prepared. Figure 3 shows the amount adsorbed as a function of time. It is seen that adsorption equilibrium is attained in ~ 10 min. The amount adsorbed on Al₂O₃ is much greater than that on 12% WO₃/Al₂O₃; under these conditions, virtually no adsorption occurs on WO₃. The weight loading on Al₂O₃ that corresponds to the plateau shown in Figure 3 is ~ 0.02%, clearly demonstrating that the adsorption/exchange component of Co derived from wet impregnation is very small.

Figure 3: Adsorption of Co²⁺ onto: Δ Al₂O₃; ○ 12% WO₃/Al₂O₃; and ● WO₃

The equilibrium adsorption results show that only a small amount of Co^{2+} ions is transferred to the solid phase. In the case of Al_2O_3 , this is expected; the experiment was conducted at a pH ~ 6 which is below its point of zero charge. The net charge on the surface is positive, and the existence of any adsorption suggests that direct exchange with surface hydroxyls is the mechanism for adsorption.

On the other hand, we see virtually no adsorption on WO_3 . At a pH of 6, the net charge on WO_3 (PZC ~ 3.6 [22]) is negative, but the very low surface area of WO_3 ($\sim 1\text{m}^2/\text{g}$ [22]) results in negligible adsorption of Co^{2+} on WO_3 .

The composite oxide shows what appears to be an intermediate behavior as far as its adsorption uptake is concerned. This result could be due to several factors. The PZC of this composite is ~ 6 [22] which would suggest that Co^{2+} ions in the bulk solution would experience only a small driving force for interaction with the surface. On the other hand, our modeling of the charge development on composite oxides is based on the simple additive contribution of each phase (based on surface area) to the measured PZC. Based on this, the WO_3 phase would be "negative" (pH preparation $>$ PZC WO_3) and adsorption should be favorable. However, the estimated surface area of the second phase is $\sim 15\text{m}^2/\text{g}$ [22] which would suggest that the measured adsorbed amount should be greater than bulk WO_3 but less than Al_2O_3 (surface area $\sim 150\text{m}^2/\text{g}$).

5.3 Pd/ Al_2O_3 / SiO_2

If alumina was uniformly distributed over the surface of the silica support used in this study, a composite with 10% Al_2O_3 would have a surface density of $2.2\text{ Al}^{3+}/\text{nm}^2$. Assuming a mean density of $6\text{ OH}/\text{nm}^2$ for silica, approximately 40% of the ionizable surface sites of pure silica would be covered by the aluminum ions, which should give rise to a significant increase in the PZC of the composite. A comparison of the measured PZC for pure silica (3.80) and the composite support (5.08) indicates, however, that the acidic function of the $-\text{SiOH}$ groups was modified to a lesser extent by the alumina clusters. The BET surface area and the adsorption properties of the composite were also only slightly modified by the second phase oxide. These facts suggest that a large part of the original silica surface remained free of alumina, the second phase oxide being probably present as small clusters deposited over a large silica surface. A rough estimate of the alumina cluster size, based on the PZC values of pure and composite oxides and the BET area of the composite [21,22] gave a value of $14 \pm 4\text{ \AA}$.

It is well documented that the pH of impregnation solutions plays an important role in catalyst preparation because it controls both the surface charge development on oxidic supports in aqueous environments and the amount of ionic solutes absorbed or exchanged by electrostatic interactions. This is true unless the ionic solute hydrolyzes to form hydroxocomplexes in solution or interactions with the surface through non-electrostatic bonds.

Palladium tetraamine cations were chosen for this study because their adsorption on both silica and alumina surfaces conforms to the electrostatically dominated mechanism [23,24]. This has been demonstrated in separate adsorption experiments using pure alumina, pure silica and a 10% alumina on silica composite. For identical impregnation conditions, it has been found that the amount of palladium adsorbed on these supports is strongly dependent on pH (Fig. 4). The cationic species of palladium exchanged onto silica and alumina are held relatively strongly, as judged by their resistance to removal by

Figure 4: The influence of the impregnation pH on adsorption of palladium tetraamine on different supports; 1 - silica; 2 - 10% alumina on silica composite; 3 - alumina.

washing with deionized water. This would require hydrolysis of the adsorbed surface complex with the formation of silanol groups, $\text{Pd}(\text{NH}_3)_4^{2+}$ and the release of OH^- ions to the solution. The equilibrium constant for this process is unfavorable.

Data shown in Fig. 4 follow the pH-dependent evolution of the surface charge on silica [25], as required by the ion exchange mechanism of adsorption. Even though the PZC of silica is about 3, the negative surface charge remains very low up to a pH of about 6 and then increases rapidly to a pH of about 10.8 - 11. Above about pH 9, silica dissolves and forms HSiO_3^- ions, which are present in increasing amounts as the pH is raised. The dramatic increase in palladium adsorption on silica and the composite on increasing the pH above 6 is in perfect agreement with the pH-controlled evolution of surface charge on silica. For equal pH values, the amount adsorbed on the alumina-bearing composite was slightly lower than that adsorbed on pure silica (for example, compare 3.06% with 2.94% at pH 10.2). This can be explained either by a decrease in the number of free sites exposed by silica or by the buffering action of alumina. Both effects contribute to a decrease in the net surface charge of the composite.

A very small amount of palladium tetraamine was adsorbed on pure alumina at pH 10.2 (0.26%) and no adsorption was found at pH 8.5 or 6. This is in agreement with the much smaller negative surface charge of alumina (as compared with silica at the same pH) [26] and also with the lower interaction energy of $\text{Pd}(\text{NH}_3)_4^{2+}$ species with the alumina surface [23].

Adsorption data alone are not sufficient to estimate the extent of partitioning of palladium between silica and alumina sites on the composite support. The large difference in adsorbed amounts of pure silica (287.6 $\mu\text{moles/g}$) and on the pure alumina (24.4 $\mu\text{moles/g}$) is very small at pH 10.2 and is obviously related to the much lower negative surface charge of the latter support at this pH. It was assumed that palladium adsorbed on the composite oxide is partitioned proportionally on the basis of the adsorptive capacities of the pure components measured at the same pH. For the composite oxide prepared at

pH 10.2 (276.3 μ moles Pd/g), calculation gives 257 μ moles Pd/g and 19.3 μ moles Pd/g, respectively, for silica and alumina components. For catalysts prepared at lower impregnation pH's, it was assumed that palladium was located only on silica sites. These figures have been further substantiated by the TPRd characterization of the composite [27].

6. CONCLUSIONS

Over the past several years, there have emerged numerous reports that have approached the subject of catalyst preparation both systematically and fundamentally. In our work, we have extended well-established principles of colloid chemistry to the systems commonly used in catalysis. The work described herein is a further attempt to establish a scientific basis for the preparation of metal-supported catalysts. We use a design scheme that is quite general and which may be applied judiciously to a large number of supported metal-oxide systems. It is not confined to catalytic studies. Possible intrinsic benefits may be found in areas such as adsorption of hazardous wastes, the stability of colloids, fabrication of ceramics, or any other materials science process related to adsorption. Advances in the area of catalyst preparation would significantly improve industry's present day approach to designing a new catalyst. Instead of formulating and testing scores of catalysts each with a slight variation in "recipe", the desired final morphology of the catalyst could be produced much more directly. As the process of catalyst design undergoes this fundamental streamline, the cost of time, materials, and effort of evaluation will be greatly reduced. We believe studies of the type described can serve as a template to replace one element in the causal chain of steps to prepare catalysts with one that has a scientific basis.

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