JOURNAL OF CATALYSIS **138**, 400–404 (1992)

Adsorption of Palladium on γ-Alumina

The impregnation of the catalytically active metal (e.g., palladium) on a support (e.g., γ-Al_2O_3) is a critical step in catalyst preparation since the variables used during the impregnation process affect the structure and activity of the catalyst. These variables are the properties of the electrolyte, the mutual interactions between the electrolyte and the support, and the properties of the support. It has been shown that the adsorption process is affected by changes in the pH (*1, 2*), ionic strength (*3*), and initial concentration (of the metal species) of the electrolyte (*4*). The effect of adding chemical ingredients on the adsorbed metal profiles (*5, 6*) and the effect of changes in impregnation pH on the Langmuir adsorption isotherm parameters have been studied (*7*). The investigation of support–electrolyte interactions has also attracted attention. It is known that alumina dissolves in highly acidic impregnation solutions (*8–10*) and that a fraction of the dissolved aluminum is readsorbed (*11*). Kinetic measurements conducted to study alumina dissolution have shown that the dissolved aluminum concentration passes through a maximum (*12*).

It has been shown recently that support properties such as X-ray crystallinity (*13*) and point of zero charge (pzc) (*14, 15*) affect the structure and activity of the catalyst. It has been proposed that the peak temperatures observed during temperature-programmed reduction (TPRd) are related to the X-ray crystallinity of the support (*13*). The adsorption and TPRd studies conducted on Al_2O_3–TiO_2 composite oxide supported Pt and Ir precursors have suggested that the difference in the pzc of the components of a composite oxide may be used to selectively impregnate one of the components (*15*). The selective ion exchange of palladium on Al_2O_3–SiO_2 composite oxides has also been studied (*16*). Therefore, investigation of the effect of support properties on the adsorption process is of interest. The objective of this study is to assess the effect of changes in the support properties, X-ray crystallinity, and pzc on the adsorption of palladium. The adsorption of palladium nitrate on three γ-aluminas of varying crystallinity and pzc was investigated.

Palladium nitrate ($Pd(NO_3)_2 \cdot xH_2O$, Pd content 41.46%, Alfa Products) was used as the source of palladium for conducting the adsorption experiments. Three types of γ-aluminas, Al_2O_3–C (Degussa Corp.), high surface area (HSA), Versal GH (LaRoche Chemicals), and low surface area (LSA) Versal GH (LaRoche Chemicals), were used in this study. While Al_2O_3–C is manufactured by the flame hydrolysis of $AlCl_3$, the Versal GH aluminas are prepared by calcining aluminum monohydrate.

The three oxides were calcined in the laboratory at 600°C for a period of 24 h. This step was performed to assure uniform thermal pretreatment for the three γ-aluminas. The BET surface area (measured using nitrogen adsorption) and pore volume (of pores less than 200 Å in size) of these materials were measured and the values are reported in Table 1.

The X-ray diffraction analyses were conducted using a vertical powder diffractometer equipped with a diffracted beam monochromator and Cu$K\alpha$ radiation (λ = 1.542 Å). The width at half height (WHH) was calculated from a Lorentzian fit of the peaks observed at 60.5 and 66.8°. The WHH is an index of the crystallite size and hence an index of the X-ray crystallinity of the oxide.

0021-9517/92 $5.00

The point of zero charge of an oxide is the pH at which the oxide has zero net surface charge. The pzc of the oxides was measured by "mass titration"; the theoretical considerations and the experimental details have been described previously (*17, 18*).

The dissolved metal concentrations were determined by inductively coupled plasma emission spectroscopy (ICPS) using a VG Elemental PlasmaQuad. The standard deviations in the measured Pd and Al concentrations were 7 μg/cm^3 and 1 μg/cm^3, respectively. The pH measurements were carried out using a Corning 255 pH meter calibrated with buffer solutions of pH 1.0 and 4.0. The standard deviation in the measured pH values was 0.06 pH units.

Palladium nitrate solutions of two concentrations, 539 and 2125 μg/cm^3, were prepared. These were designated standard solutions and their pH values were measured to be 2.0, and 1.5, respectively. The pH of the standard solutions was adjusted by using either HNO_3 (3 *N*) or NH_4OH (0.5 *N*). The palladium nitrate solution tended to precipitate when the pH was adjusted to a value outside the range 1.5 to 2.5. The palladium nitrate solutions (24 cm^3) were contacted with alumina (0.09 g) and allowed to equilibrate for a period of 24 h. A Burrell wrist-action shaker was used for this purpose. Auxiliary experiments conducted during this study showed that adsorption equilibrium was attained within 24 h. The suspensions were centrifuged (International Clinical Centrifuge Model 31070H) and the pH, Al, and Pd content of the solutions (at equilibrium) were measured.

The X-ray diffraction patterns for the three aluminas showed patterns consistent with the γ phase of Al_2O_3, i.e., peaks at 60.5 and 66.8°. The WHH values for the peaks observed at 60.5 and 66.5° are presented in Table 1. The pzc's of Al_2O_3–C, LSA, and HSA were determined to be 4.80, 8.50, and 7.20, respectively.

Alumina dissolves in the acidic palladium nitrate solution and the Al concentration in the liquid phase increases during the adsorption of Pd. The pH of the impregnation solution increases as Al dissolves. The dissolved Al concentration and pH at equilibrium are shown as a function of the initial pH in Table 2. It has been proposed that the concentrations of catalytic precursors on the support may be evaluated by considering two contributions, the pore-filling component (Pd_{Pore}) and the adsorbed component (Pd_{Ads}) (*2*). The pore-filling and adsorption contributions were calculated and the values are presented in Table 3. Note that the pore-filling component is relatively insignificant compared to the adsorbed component because the final concentration of Pd in the electrolyte is low.

TABLE 1

Surface Area, Pore Volume, Density, and WHH for the Three γ-Aluminas Used

Type	Bulk density (g/cm^3)	BET surface area (m^2/g)	Pore volume (cm^3/g)	WHH for the diffraction peak at	
				60.5°	66.8°
Alumina–C	0.50	114	0.15	1.45	3.15
LSA	0.56	154	0.40	1.61	5.07
HSA	0.60	223	0.54	2.33	6.00

It was recently reported that the X-ray diffraction pattern can be used to characterize the crystallinity of alumina (*13, 19*). The peaks observed at 60.5 and 66.8° are characteristic of γ-Al_2O_3 and hence were chosen for further analysis. The WHH values reported in Table 1 show that the peaks are broader in the case of HSA and narrower in the case of Al_2O_3–C. Generally less crystalline materials show broader peaks and hence the relative order of crystallinity may be written as: (least crystalline) HSA < LSA < Al_2O_3–C (most crystalline).

It has been proposed that the more crystalline forms of Al_2O_3 may be more resistant to dissolution (*19, 20*). Under the conditions studied (Table 2), the maximum amount of Al dissolution is observed when HSA alumina is contacted with a solution having Pd concentration of 539 μg/cm^3 and pH 1.57.

TABLE 2

Dissolved Al Concentration and Equilibrium pH

Initial pH	Al_2O_3–C		HSA Versal GH		LSA Versal GH	
	Diss. Al conc. ($\mu g/cm^3$)	Equi. pH	Diss. Al conc. ($\mu g/cm^3$)	Equil. pH	Diss. Al conc. ($\mu g/cm^3$)	Equil. pH
Initial concentration of solution = 2125 $\mu g/cm^3$						
0.98	53	1.02	233	1.03	67	1.02
1.49	43	1.53	177	2.02	50	1.63
2.06	31	2.28	79	4.26	39	3.34
2.48	25	3.42	60	4.26	31	4.25
Initial concentration of solution = 539 $\mu g/cm^3$						
1.57	102	1.69	275	4.15	122	1.83
2.00	70	2.31	86	4.17	93	4.02
2.50	56	4.03	24	4.75	31	4.26

Here approximately 14.1% of the added Al (as Al_2O_3) goes into solution. The data reported in Table 2 also show that larger amounts of Al^{3+} are released into the solution phase as the electrolyte becomes more acidic.

The data shown in Table 2 indicate that the equilibrium pH is higher than the initial pH of the impregnation solution. This observation is in agreement with the mechanism proposed for alumina dissolution (*12*). These investigators have proposed that the alumina surface is hydrated upon immersion in the solution and Al^{3+} is released in the presence of H^+:

$$Al_2O_3 + 3H_3O^+ \rightarrow 2Al(OH)_3 + 3H^+ \rightleftharpoons 2Al^{3+} + 3H_2O + 3OH^-. \quad (1)$$

The equilibrium pH values can be used in conjunction with the observed dissolved Al concentrations to rank the ease of dissolution as follows: (difficult) Al_2O_3–C < LSA < HSA (facile). The X-ray crystallinity and Al^{3+} dissolution data support the hypothesis that the more crystalline forms of alumina dissolve to a lesser extent when acidic impregnation solutions are used. Table 2 also shows that, at a given pH, the dissolved Al^{3+} concentration is lower when the initial Pd concentration of the impregnation solution is higher. Also the change in pH (i.e., equilibrium pH − initial pH) resulting from Al dissolution is generally lower when the Pd concentration is higher. This suggests that the addition of palladium nitrate buffers the solution and decreases the amount of Al^{3+} released into the aqueous phase.

The amount of Pd_{Ads} (percentage by weight of alumina) is shown in Table 3. It is observed that the addition of acid (HNO_3) or base (NH_4OH) increases the amount of Pd adsorbed at equilibrium. The amount of Pd adsorbed is lowest when the pH is 2.0, i.e., when no acid or base added. It is important to recognize that the addition of HNO_3 or NH_4OH also changes the ionic strength of the electrolyte. The data presented in Table 3 show the combined effect of changes in pH and ionic strength.

Based on the pK_{eq} values reported in the literature (*21, 22*), drastic changes in the concentrations of the Pd^{2+}, $PdOH^+$, and $Pd(OH)_{2(aq)}$ species are expected when the pH varies between 1.5 and 2.5. This suggests that an increase in the amount of Pd adsorbed due to the addition of acid or base may be due to the changes in the concentration of the Pd species in the electrolyte. Our interest in the adsorption phenomenon is focused toward correlating the properties of γ-Al_2O_3 with the amount of Pd adsorbed. This analysis is presented in the following paragraphs.

TABLE 3

Pore Filling and Adsorbed Pd Loadings Resulting from Impregnation Solutions Having Initial Pd Concentration of 539 $\mu g/cm^3$

Alumina	Initial pH	Pd_{Pore} loading (%) ($\times 10^3$)	Pd_{Ads} loading (%)
Al_2O_3–C	1.57	0.3	12.63
Al_2O_3–C	2.00	3.9	6.59
Al_2O_3–C	2.50	0	13.16
HSA	1.57	12.3	8.64
HSA	2.00	24.1	4.29
HSA	2.50	20.3	5.68
LSA	1.57	26.4	2.33
LSA	2.00	26.1	2.45
LSA	2.50	23.3	3.63

It has been suggested that the chemical attack resulting in alumina dissolution is the fundamental step for adsorption of ions such as $PtCl_6^{2-}$ and Ni^{2+} on γ-Al_2O_3 under highly acidic conditions (*8, 9, 13*). The validity of this proposal was examined for the adsorption of the Pd^{2+} ion. No correlation was observed between the amount of Pd adsorbed and the dissolved Al concentration at constant initial pH. This suggests that, unlike the adsorption of H_2PtCl_6 or $Ni(NO_3)_2$, the acid attack on Al_2O_3 is not the fundamental step in the adsorption of palladium. Recall that alumina dissolution is related to the X-ray crystallinity. It may therefore be proposed that the amount of Pd adsorbed does not correlate with X-ray crystallinity of alumina.

It is known that the oxide has a net positive surface charge when the pzc of the oxide is greater than the pH of the electrolyte (*23*). The net surface charge is the difference between the number of positively charged sites and the number of negatively charged sites. The net surface charge becomes increasingly positive as the pH becomes substantially lower than the pzc (*24*). The surface charge–pH considerations suggest that the number of negatively charged sites decreases when the difference between the pzc of the oxide and the pH of the electrolyte increases. Since Pd^{2+} ions adsorb on negatively charged sites, the amount of Pd adsorbed should decrease when the pzc of the oxide increases. This hypothesis was examined by comparing the amounts of Pd adsorbed on different aluminas.

The variation in the amount of Pd adsorbed as a function of the pzc of the oxide at constant initial pH is presented in Table 4. These data support the hypothesis that the amount of Pd adsorbed decreases when the pzc of the oxide increases. Alumina–C has the lowest pzc; at a given pH, the amount of Pd adsorbed on Al_2O_3–C is larger than that adsorbed on HSA or LSA alumina. This suggests that pzc (rather than support crystallinity) is the dominant support property that affects the adsorption of Pd. The data reported in the present study suggest that the amount of Pd adsorbed at equilibrium can be varied by changing the speciation of the palladium nitrate electrolyte and/or by changing the pzc of the support.

TABLE 4

Relationship between Amount of Pd Adsorbed and the pzc of the Support

Type of alumina	pzc	Pd_{Ads} loading (%) at		
		pH 1.5	pH 2.0	pH 2.5
Al_2O_3	4.80	12.63	6.59	13.16
HSA	7.20	8.64	4.29	5.68
LSA	8.50	2.33	2.45	3.63

This study shows that Al^{3+} ions are released into the electrolyte when γ-Al_2O_3 is impregnated with an aqueous solution of palladium nitrate. The amount of Al released into solution varies with the X-ray crystallinity of the support. The more crystalline forms of alumina show lower amounts of dissolution. Palladium nitrate buffers the solution and lesser amounts of Al^{3+} are released into solution when the initial concentration of Pd in the electrolyte increases.

This study shows that the adsorption of Pd on alumina can be increased by adding either an acid or a base to the impregnation solution. The amount of Pd adsorbed does not correlate with the X-ray crystallinity of the oxide. The pzc of the oxide appears to be the most significant property that determines the amount of Pd adsorbed. Oxides having higher pzc's show lower tendency toward Pd adsorption.

ACKNOWLEDGMENTS

The authors thank Dr. K. Otto for critically reading the manuscript, Mr. R. J. Kudla for the BET analysis, Ms. K. Ivanovic for the ICPS analysis, and Mr. J. Knipp and Mr. D. Mudd of LaRoche Chemicals for providing the HSA and LSA Versal GH alumina samples.

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Received February 20, 1992; revised June 9, 1992

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