# Why ion-doped, PZC-altered silica and alumina fail to influence platinum adsorption

J. Korah, W.A. Spieker, and J.R. Regalbuto *

*Department of Chemical Engineering, University of Illinois at Chicago, 810 S. Clinton Street,*
*Chicago, IL 60607, USA*

Received 22 April 2002; accepted 1 October 2002

The point of zero charge (PZC) of common oxide catalyst supports such as alumina and silica can be altered by doping with anions such as $Cl^-$, which lower the ZPC, or cations such as $Na^+$ or $K^+$, which raise the PZC. In a prior work it was shown that such alterations did not influence the properties of either support toward the adsorption of either cationic amine or anionic chloride complexes of Pt(IV) [1]. This follow-up work explored the hypothesis that in the pH range of interest (low pH over cation-doped silica, high pH over anion-doped alumina) the dopant is dissolved and the surface behaves as pure.

The PZCs of doped silica and alumina washed in acidic, neutral, and basic solutions was measured by the EpHL (equilibrium pH at high loading) technique. Repeated acid washes of $K^+$-doped, PZC-raised silica quickly brought the PZC back to that of the pure oxide, and the same was observed for basic washed, PZC-lowered $Cl^-$-doped alumina. Thus, ion doping of silica and alumina does not appear to create irreversible changes in the materials' PZC and cannot be used to influence adsorptive properties.

**KEY WORDS:** ion doping; silica; alumina; platinum; PZC; adsorption; electric double layer.

## 1. Introduction

There have been many recent advances in the understanding of noble metal catalyst impregnation, dating from the landmark postulation of Brunelle that the adsorption of noble metal complexes onto common oxide supports was essentially coulombic in nature [2]. The hydroxyl groups that populate oxide surfaces become protonated and so positively charged or deprotonated and negatively charged below a characteristic pH value. This pH, at which the surface is neutral, is termed the point of zero charge (PZC). Brunelle cited many instances in which oxides placed in solutions at pHs below their PZC would adsorb anions such as hexachloroplatinate, $[PtCl_6]^{2-}$, while at pH values above their PZC would adsorb cations such as tetra-amonium platinate (TAP), $[(NH_3)_4Pt]^{2+}$ [2]. This electrostatic mechanism was semi-quantitatively developed by another landmark work, that of Contescu and Vass [3], who studied the adsorption of $[PdCl_4]^{2-}$ and $[(NH_3)_4Pd]^{2+}$ over alumina at low and high pH, respectively. Much more work on the experimental verification and quantification of this "physical" adsorption process has been conducted in our own laboratory for the chloroplatinic acid ($H_2PtCl_6$, or CPA)/alumina system [4–7]. The revised physical adsorption (RPA) model [7], with which all known sets of Pt/alumina adsorption data can be satisfactorily simulated with no adjustable parameters, is a result of these efforts. Most recently, the mechanism of adsorption has been probed at the molecular scale using techniques such as $^{195}$Pt NMR and EXAFS to study the coordination chemistry of dissolved and adsorbed complexes arising from CPA [8,9, and references therein].

An exciting application of this fundamental understanding, for adsorption systems that follow an electrostatic mechanism, is the potential to alter the adsorptive properties of the support by changing the support PZC. This possibility is suggested by several earlier works which demonstrate how doping an oxide surface with even low levels of ions can drastically alter the oxide's PZC. For alumina it has been shown that the PZC can be lowered from 8 to 4.8 by doping with chloride [10]. The PZC of silica was raised from 3.25 to 4.8 by doping with $Na^+$ [11]. In general, cations increase the PZC of oxides and anions decrease it.

The potential impact of PZC-altered surfaces on adsorptive properties was recently assessed with the RPA model [1]. Figure 1 presents predictions from this model for the uptake of CPA and TAP versus pH at constant metal concentration onto silica, alumina, and two hybrid substrates. In figure 1(a), for CPA, uptake is strongest over alumina, which possesses a PZC of about 8–8.5 [6,7], and does not occur over silica, which has a PZC of about 3.5–3.8 [1]. The hybrid surface, shown as the dashed line with intermediate behavior, can be produced in theory at least, either by doping alumina with chloride down to a PZC of 6, or doping silica with $K^+$ up to a PZC of 7 [1]. In the basic pH range, seen in

---

* To whom correspondence should be addressed.
E-mail: jrr@uic.edu

1011-372X/03/0100-0123/0

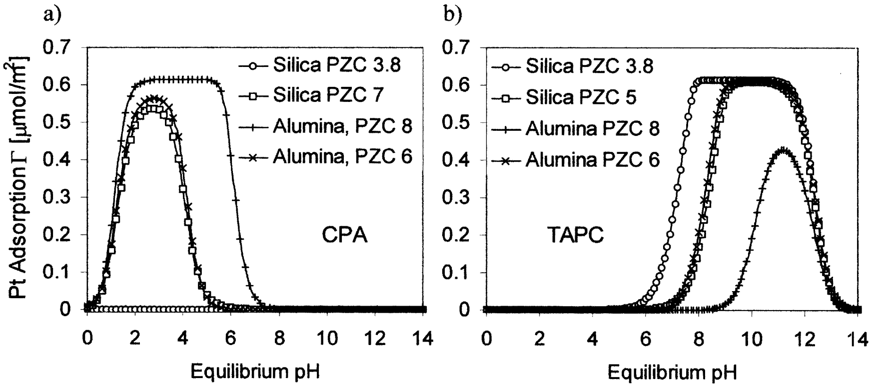

Figure 1. RPA simulation of Pt uptake over amorphous silica, PZC = 3.6, alumina, PZC = 8.5, and an ion-doped alumina or silica surface with PZC = 5.6.

figure 1(b), TAP adsorption occurs most strongly on silica and weakly on alumina. The intermediate uptake curves can be produced by modeling alumina with a PZC alteration to 6 by $Cl^-$ doping, or with silica PZC-altered to 5 by $K^+$ doping.

The attempt to make silica behave as alumina, and vice versa, failed [1]. The adsorption behavior of the doped supports was identical to those of the undoped supports in both cases. The "good news" is that even impure oxide supports, such as precipitated silicas that typically contain a high level of Na impurity and have PZCs above 6, can be treated as pure oxides (that is, using a common, well-known PZC value) in the RPA model, which renders the model all the more predictive. The "bad news", however, is that ion doping over silica and alumina does not beget the ability to alter their adsorptive properties, at least for ionic Pt complexes. Perhaps this explains why no such success has been reported in the literature to date, including from either of the groups who had initially reported PZC shifts with ion doping, and had expressed this hope.

In our earlier paper we hypothesized that the failure of the dopants to influence adsorptive properties was due to their dissolution in the pH range of interest [1], despite the fact that the doped oxides were calcined at 500 °C prior to being contacted with the solutions. It was hoped that the high-temperature calcination might somehow "fix" the dopants to the surface, rendering the PZC change irreversible. In this short communication, we demonstrate that dissolution does in fact occur in the pH range where the alteration is needed. We have washed the doped, calcined, PZC-altered oxides in various pH solutions, measured the PZCs of the washed samples, and, where possible, have monitored the washings for the dopant ions. The ultimate result is that the lowering of oxide PZC by anions is not irreversible in basic solutions, and the raising of PZC by cations is not irreversible in acidic solutions. After washes in these respective solutions, the PZCs of both oxides return to their pure values as the dopant is removed.

## 2. Experimental

Cabosil amorphous fumed silica with a surface area of 380 $m^2/g$ and LaRouche gamma alumina with a surface area of 250 $m^2/g$ were used as supports. Potassium nitrate was used to dope the silica, in an aqueous solution with concentration corresponding to 1 potassium ion per 8.2 surface hydroxyl groups on the surface of silica. The solution was added to fill the pore volume of silica, 1.7 mL/g. For alumina, the pore volume was 2.0 mL/g. The concentration of ammonium chloride corresponded to a loading was about 1 chloride ion per 20 surface hydroxyl groups on the surface of alumina.

After ion doping by impregnation, the silica and alumina were dried overnight at room temperature, then dried for 3 h at 110 °C, and finally calcined for 5 h at 500 °C in air in a muffle furnace. Three sets of the doped silica and alumina were then washed with different pH solutions three times. For the washing procedure, a volume of solution about 10 times in excess of the pore volume was employed, and after contacting the mixtures were shaken for 1 h and then filtered. The filtered samples were dried overnight and calcined for 5 h at 500 °C in air. A first set of each oxide was washed three times with deionized water (DIW) with a pH of about 5.8. Second sets were also washed three times with an acidic $HNO_3$ solution at a pH of 2. The third set of silica was washed with a basic solution of $NH_3OH$ at a pH of about 9, while to use a pH high enough above the PZC, for the third set of alumina a solution of NaOH at about a pH of 12 was employed.

PZC measurements were made by the EpHL (equilibrium pH at high loading) technique [12]. In this method, solutions of various initial pH are contacted with oxides by pore filling. The final pH, measured using a spear-tip electrode for semi-solids [12], is invariant over a wide range of pH; this plateau corresponds to the PZC. Sample EpHL results for the pure alumina and silica samples used in this work are shown in figure 2. The PZC of the pure alumina sample is seen to be about 8.3, and that of pure silica about 3.3. (The left-most

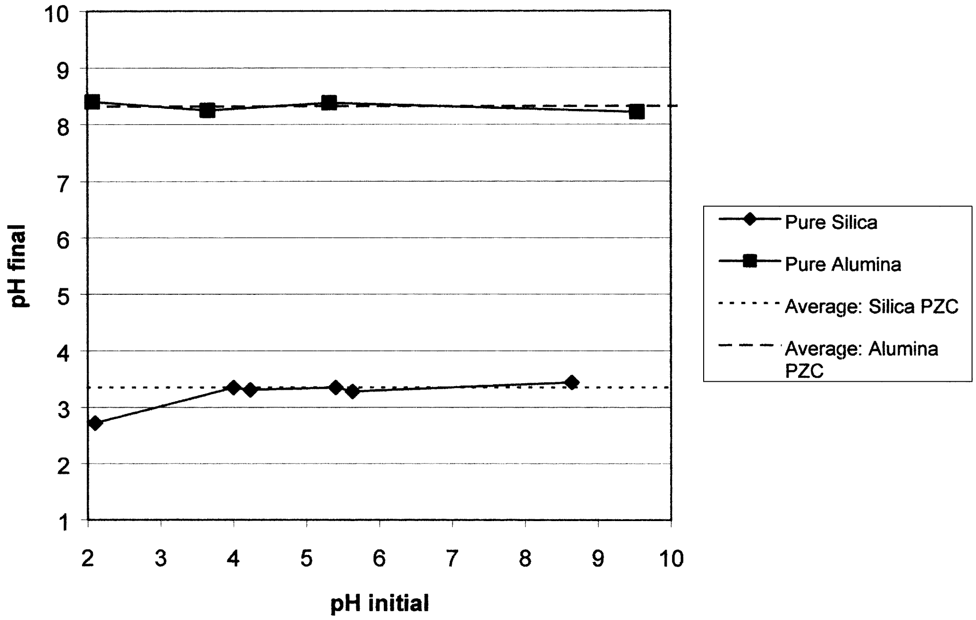

Figure 2. EpHL results for PZC measurement of pure alumina and silica.

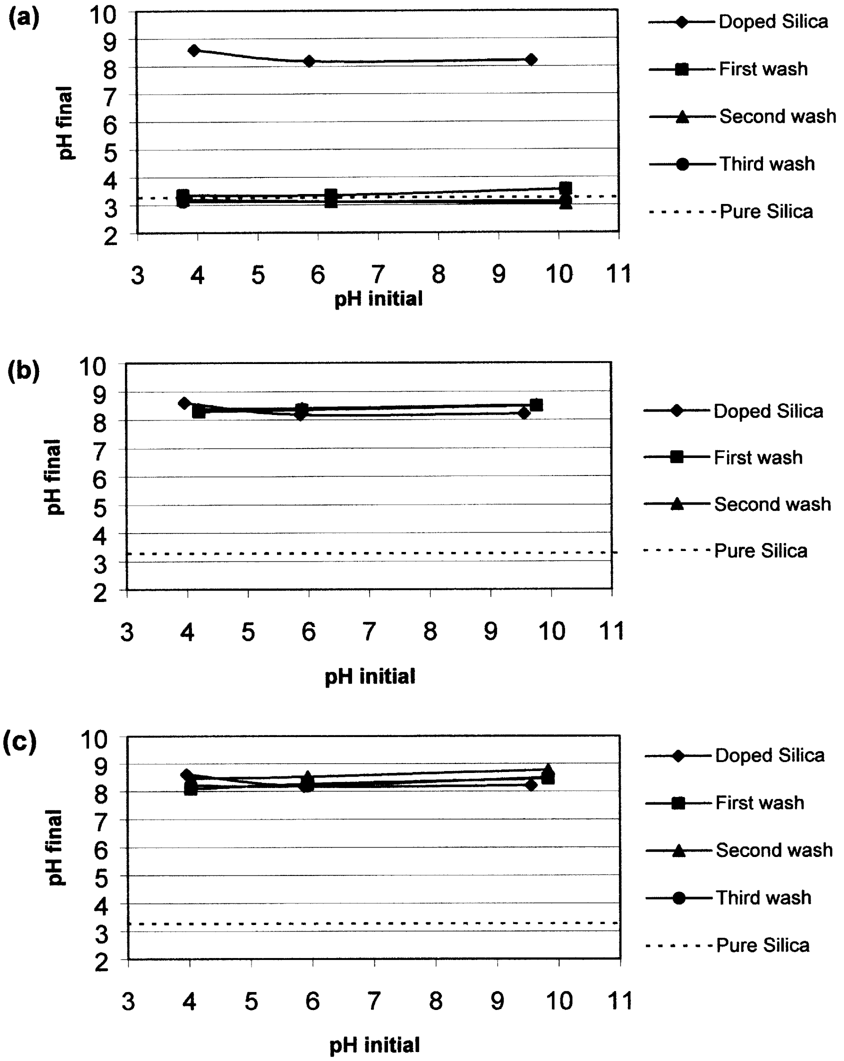

Figure 3. EpHL results for silica, washed in solutions which were (a) acidic, (b) neutral, and (c) basic.

point for the silica sample is off of the plateau, as expected [12], and was not used in the PZC calculation.) The reproducibility of successive measurements is about ±0.3 pH unit.

Table 1
Summary of PZC measurements

| Silica | PZC | | |
|---|---|---|---|
| Unwashed | $K^+$ doped: 8.3 ± 0.3 (pure: 3.3 ± 0.3) | | |
| Wash pH: | Acidic | Neutral | Basic |
| Wash 1 | 3.4 | 8.4 | 8.3 |
| Wash 2 | 3.1 | 8.4 | 8.6 |
| Wash 3 | 3.1 | – | 8.3 |
| Alumina | PZC | | |
| Unwashed | $Cl^-$ doped: 6.7 ± 0.3 (pure: 8.3 ± 0.3) | | |
| Wash pH: | Acidic | Neutral | Basic |
| Wash 1 | 6.5 | 6.7 | 8.1 |
| Wash 2 | 6.8 | 6.5 | 8.1 |
| Wash 3 | 6.6 | 6.5 | 8.1 |

## 3. Results and discussion

Figure 3 shows EpHL results ($pH_{final}$ versus $pH_{initial}$) for the acid-washed (figure 3(a)), DIW-washed (figure 3(b)), and base-washed silica (figure 3(c)). The PZC values for each case, determined as the average of the three pH measurements for each sample, are given in table 1. The PZC of the K-doped silica is 8.4, well above that for pure silica, about 3.5, seen in figure 2. This high PZC is unaltered after repeated washes in either DIW or basic solutions. However, after an initial wash with acid solution (0.01 M $HNO_3$), the PZC drops back almost to that of the pure silica. A second wash brings the PZC fully back to the pure oxide value. A third wash results not in a further lowering of the PZC, but the pure oxide PZC again. This trend is consistent with the removal of the cationic dopant by the acid wash.

The washings were monitored for $K^+$ by ICP. Corresponding to the PZC results, the neutral and base washings showed no $K^+$, while $K^+$ was detected in the

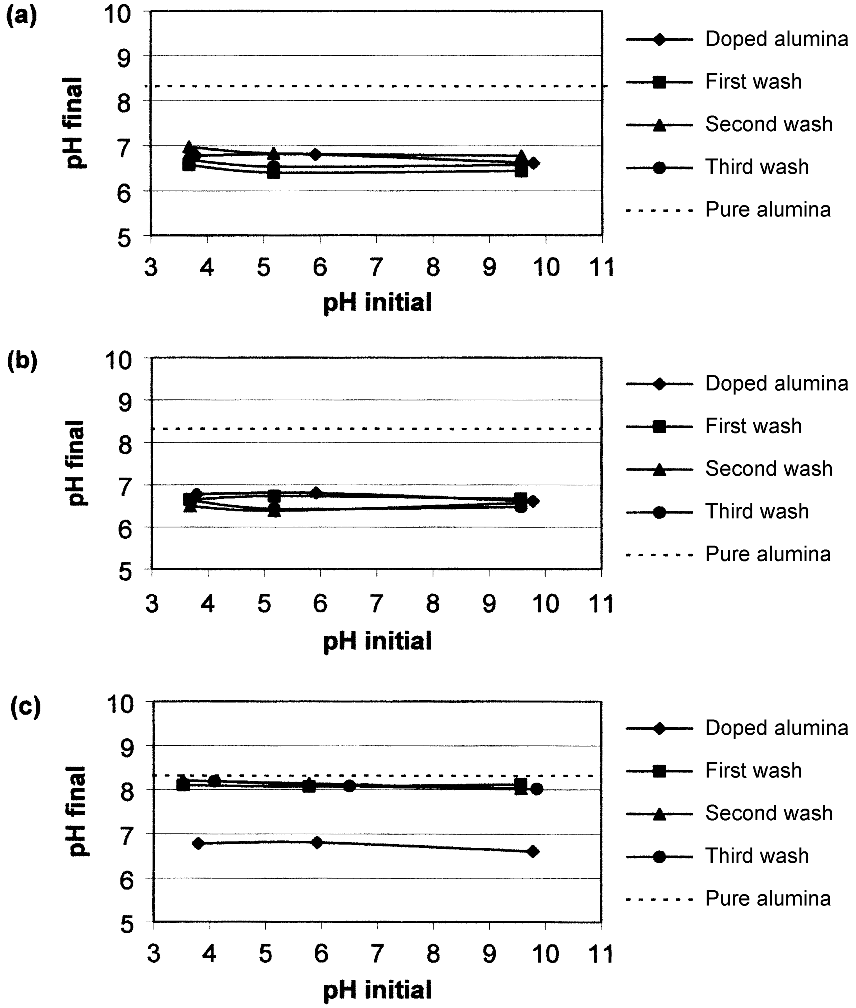

Figure 4. EpHL results for alumina, washed in solutions which were (a) acidic, (b) neutral, and (c) basic.

acid washings at a concentration roughly corresponding to the amount added to the silica during the preparation.

Both sets of results demonstrate that $K^+$ can be dissolved from silica in an acidic medium, even after the doped silica had been calcined at 500 °C. It was in the acidic pH range that the adsorption of $[PtCl_6]^{2-}$ was attempted over the K-doped, PZC-raised silica, with no success [11]. The present results suggest that the $K^+$ dopant was removed from the surface upon contact with the acid solutions and the resulting surface behaved like pure silica.

The analogous trend is seen for the Cl-doped alumina samples. A summary of the PZC values for the acid-, neutral-, and base-washed samples are included in table 1. The EpHL results are presented in figure 4 for the acid-washed (figure 4(a)), DIW-washed (figure 4(b)), and base-washed alumina (figure 4(c)). In this case, the PZCs are virtually unchanged after repeated washes in acidic and neutral solutions, suggesting that the dopant remains affixed to the surface under these conditions. However, the initial wash in a pH 12 NaOH solution brought the PZC all the way up to that of pure alumina (table 1, figure 2), and subsequent washings did not alter the PZC any further. This evidence is consistent with the facile removal of $Cl^-$ ions in the basic solution, even though the Cl-doped alumina had been calcined at 500 °C.

It had been thought that due to its lower PZC, the Cl-doped alumina sample might adsorb TAP more strongly than pure alumina [11]. The dissolution of $Cl^-$ in basic solution appears to yield an essentially pure alumina surface, with the same adsorptive properties as the undoped sample. This is not to say, however, that finished catalysts prepared from pure and $Cl^-$-doped alumina (or pure and $K^+$-doped silica) would necessarily exhibit the same activity. In the finished catalysts any dissolved $K^+$ and $Cl^-$ dopant that redeposits on the surface might indeed influence activity and selectivity.

While the Pt adsorptive properties of these ion-doped, PZC-altered silica and alumina samples did not change, we have achieved some success in "impregnation engineering" with activated carbons [13]. The PZC of activated carbon appears to be irreversibly altered by oxidative pretreatments. Furthermore, with respect to the adsorption of anionic and cationic Pt complexes, an unoxidized carbon with a PZC of 9 behaves similarly to alumina, and that of a severely oxidized carbon with a PZC of 3.0 behaves as does silica. The incorporation of oxygen-containing functional groups into the carbon surface is, of course, a quite different situation than the alteration of existing groups with ionic dopants. We are currently surveying other materials and other mechanisms in which the PZC might also be irreversibly changed and the adsorptive properties so altered.

## References

[1] W.A. Spieker and J.R. Regalbuto, Stud. Surf. Sci. Catal. 130 (2000) 203.
[2] J.P. Brunelle, Pure Appl. Chem. 50 (1978) 1211.
[3] C. Contescu and M.I. Vass, Appl. Catal. 33 (1987) 259.
[4] A. Shah and J.R. Regalbuto, Langmuir 10 (1994) 500.
[5] N. Santhanam, T.A. Conforti, W.A. Spieker and J.R. Regalbuto, Catal. Today, 21 (1994) 141.
[6] J.R. Regalbuto, A. Navada, S. Shadid, M.L. Bricker and Q. Chen, J. Catal. 184 (1999) 335.
[7] W.A. Spieker and J.R. Regalbuto, Chem. Eng. Sci. 56 (2000) 2365.
[8] B. Shelimov, J.-F. Lambert, M. Che and B. Didillon, J. Mol. Catal. 158 (2000) 91.
[9] W.A. Spieker, J. Liu, X. Hao, J.T. Miller, A.J. Kropf and J.R. Regalbuto, Appl. Catal. A: Gen., in press.
[10] J.A. Mieth, J.A. Schwarz, Y.-J. Huang and S.C. Fung, J. Catal. 122 (1990) 202.
[11] K.Ch. Akratopulu, L. Vordonis and A. Lycourghiotis, J. Catal. 109 (1988) 41.
[12] J. Park and J.R. Regalbuto, J. Coll. Interf. Sci. 175 (1995) 239.
[13] J.R. Regalbuto, M. Schrier, X. Hao, W.A. Spieker, J.G. Kim, J.T. Miller and A.J. Kropf, Stud. Surf. Sci. Catal. 143 (2002) 45.