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A fundamental study of Pt impregnation of carbon: Adsorption equilibrium and particle synthesis

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ABSTRACT

To determine whether the method of “strong electrostatic adsorption” (SEA) can be extended to the preparation of carbon-supported Pt catalysts, a series of carbons of different type (activated, black, and graphitic) with different surface areas and points of zero charge (PZC) has been studied. Cationic Pt tetraammine, $[(NH_3)_4Pt]^{2+}$, was adsorbed over low- and mid-PZC carbons in the high pH range, while anionic hexachloroplatinate (IV), $[PtCl_6]^{2-}$, was adsorbed over high-PZC carbons in the low pH range. Adsorption equilibrium was determined by measuring pH and metal concentration in the impregnation solution before and after contacting with the carbon supports. Filtered, dried materials were reduced in hydrogen, and the Pt particle size was characterized by Z contrast imaging.

Electrostatic adsorption occurs at short contact time (1 h) for both Pt anions and cations. The adsorptive behavior of all carbons of like PZC is the essentially the same, independent of type and surface area. There are pH optima at which electrostatic adsorption is strongest; a sharp maximum occurs for anions in the low pH range at pH 2.9, while the high pH optimum for cations is pH 12. To attain the required final values, pH buffering by the surface, a phenomenon not sufficiently appreciated in the literature, has to be overcome. Particles synthesized by SEA are normally in the 1–2 nm range and are as small as or smaller with narrower size distributions than by other methods, especially at high metal loadings.

Results also reveal a longer time scale, reductive mechanism that occurs with Pt(IV) chlorides over carbon at low pH, which mitigates the need for precise pH control if the contact time is long, and might explain the small particle sizes obtained by dry impregnation with the $[PtCl_6]^{2-}$ complex. This mechanism will be more fully explored in future work.

1. Introduction

In efforts to help turn the art of catalyst preparation into science, we have developed the method of “Strong Electrostatic Adsorption” (SEA) as a simple, rational approach to synthesize highly dispersed supported metal catalysts [1,2]. The method is based on an electrostatic mechanism [3] in which the (typically hydroxyl) functional groups on the support surface can be protonated and deprotonated and so positively or negatively charged as a function of pH relative to the point of zero charge (PZC). At the pH of strongest interaction, oppositely charged metal coordination complexes adsorb in a well-dispersed monolayer, and the high dispersion of the precursor phase is retained as the precursor is reduced to metal. To date, the electrostatic mechanism has been demonstrated for noble and base metal coordination complexes, including anionic Pt chlorides (and related hydrolysis complexes) over alumina at low pH [4], and at high pH, cationic Pt tetraammines over silica [5,6] and other noble and base metal ammines over amorphous [7] and mesoporous [8] silicas. Electrostatic adsorption was suggested to be the reason for Pt and Cu overexchange in low Al zeolites [9].

The various forms of carbon (activated, blacks, and graphite) comprise a versatile set of support materials especially for robust operation in liquid phase reactions such as hydrogenations in the pharmaceutical industry or new applications in the conversion of carbohydrates to hydrocarbon biofuels [10,11].

Numerous publications suggest that an electrostatic mechanism plays a role in the adsorption of metal coordination complexes with carbon surfaces, starting with the electrostatic “equilibrium adsorption” studies of molybdate uptake onto carbons of various PZCs [12]. Unoxidized black and activated carbons have PZCs around 9. Unoxidized carbon surfaces contain little oxygen groups but can become positively charged by protonation of the pi bonds in aromatic rings [13,14]. Introducing oxygen functional groups through various liquid or gas phase treatments lowers the PZC by a few to many pH units. Low PZC surfaces have functional groups such as carboxylic acids that deprotonate and become negatively charged at pH values above their PZC.

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Untreated graphitic carbons have mid- to low PZCs [12,14,15]. By altering the PZC of carbons in a systematic manner, the adsorptive properties of carbon surfaces might be controlled [14,15].

In a comprehensive review in 1997 by Radovic and Rodriguez-Reinoso, electrostatic adsorption is presented as the centerpiece of carbon catalyst preparation [14]. Consistent with electrostatic adsorption, several studies indicate that less severe oxidation (and correspondingly higher PZCs) leads to greater uptake of hexachloroplatinate (IV) anions ($[PtCl_6]^{2-}$, commonly referred to as chloroplatinic acid, or CPA) [16–19]. Heat-treated carbon, presumably with less surface oxygen and higher PZCs, adsorbs more CPA than oxidized carbon [16,20]. Chloroplatinate adsorption isotherms indicated that the interactions of the metallic precursor with the carbon surface were higher for carbons of low acidity (and presumably higher PZC) [21]. Surface oxygen groups, which lower PZC, have been reported to favor the anchoring of cationic platinum tetraammine ($[(NH_3)_4Pt]^{2+}$, or PTA) [14,22].

On the other hand, even after Radovic and Rodriguez-Reinoso's comprehensive review, it has been reported that increasing oxygen groups on the carbon surface had no effect on PTA uptake [23,24] or CPA uptake [24,25]. In other reports, increasing surface O yielded higher dispersion with CPA [16,27]. In yet other work, surface oxidation had a negative effect on dispersion using PTA [28,29]. Numerous authors have cited a reactive interaction of CPA with carbon [16,18,21,23,25,30,31]. There still does not appear to be a general consensus of the electrostatic or other mechanisms by which common Pt precursors interact with carbon surfaces. That common understanding is the goal of this study.

Results from our preliminary investigation over activated carbons are reproduced in Fig. 1[15]. The qualitative trends of electrostatic adsorption are indeed seen; the carbon with the highest PZC (unoxidized) adsorbs the most anions (Fig. 1a). That with the lowest PZC adsorbs the most cations (Fig. 1b). A carbon with an intermediate PZC displays intermediate uptake in each regime. In both pH regimes, the uptake – pH curves are volcano-shaped, which is a further indication of electrostatic adsorption [3].

However, there are several notable quantitative differences from a purely electrostatic model. The trends of CPA and PTA uptake over surfaces of different PZC from the "Revised Physical Adsorption" (RPA) model [3] are shown in Fig. 1c. Since ammine complexes adsorb with two hydration sheaths intact, instead of one for the anions [32], the cationic uptake is inherently about half that of the anions. In each pH regime, the curves as a function of PZC are regularly spaced volcano-type curves in which adsorption increases as pH moves away from the PZC and the surface charge builds up, but decreases at pH extremes as high ionic strength decreases the adsorption equilibrium constant [3]. In the low pH regime, a PZC 2.5 (Fig. 1b) carbon adsorbs CPA, whereas the RPA model predicts it should not. In the upper pH regime, the maximum uptake of all three carbons is only about half that anticipated from the RPA model [3].

Using the electrostatic mechanism as a benchmark, this paper presents a systematic study of the mechanism of Pt uptake over a variety of carbons (activated, blacks, and graphites) with a variety of PZCs, in an attempt to discern between electrostatic and reactive components of the metal complex–carbon surface interaction and

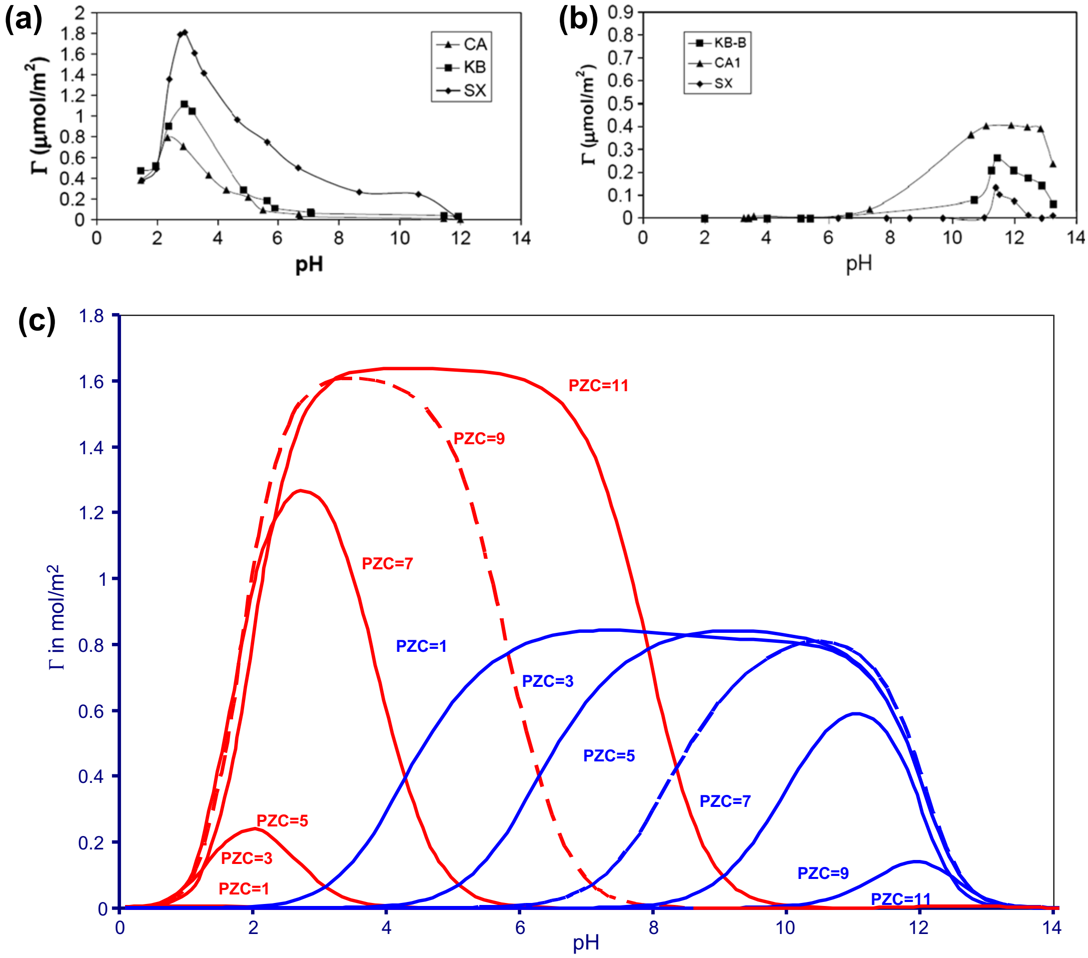

Fig. 1. Pt uptake over carbons of various PZCs versus final pH (500 m^2/L and 200 ppm CPA or 1000 m^2/L and 200 ppm PTA: (a) CPA experimental results, (b) PTA experimental results, and (c) Simulation of uptake of CPA (lower pH range) or PTA (higher pH range) versus pH for various PZC materials (Δpk 4, various PZC, $N_S = 5\ OH/nm^2$).