Synthesis of Ag Nanoparticles on Oxide and Carbon Supports from Ag Diammine Precursor

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Abstract

To determine whether the method of “strong electrostatic adsorption” (SEA) can be extended to the preparation of uniform and highly dispersed supported Ag catalysts, the adsorption of silver diammine, $\text{Ag}(\text{NH}_3)_2^+$, also known as Tollen’s reagent, has been examined over five supports (i.e., SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 , Nb_2O_5 , and carbon) with different surface areas and PZCs. The speciation of Ag in solution was followed by UV-vis spectroscopy, Ag uptake as a function of the solution pH was determined by atomic absorption, and Ag particle size was determined by powder XRD and STEM.

At the Ag concentrations, pH, and surface loadings employed, silver diammine complexes convert into soluble $\text{Ag}(\text{H}_2\text{O})_2^+$ aquo complexes below pH 11 and hydrolyze to insoluble Ag_2O above pH 11. The deposition of either Ag species over carbon at any pH appears to be reactive and results in large particles. The silver aquo complexes appear to adsorb via ion exchange near the PZC of alumina, zirconia, and niobia but not silica, while the silver diammine complexes appear to adsorb electrostatically at high pH over all the oxides tested - niobia, silica, zirconia, and alumina in the order of ascending PZC. Niobia, which has the lowest PZC, adsorbs the highest surface density of Ag via both mechanisms. The particles obtained via electrostatic adsorption of $\text{Ag}(\text{NH}_3)_2^+$ at high pH are somewhat smaller than those formed from $\text{Ag}(\text{H}_2\text{O})_2^+$ ions at the lower pH values. In the absence of ammonia in solution at high pH, deposition of Ag aquo complexes occurs via surface precipitation and gives large particles. In sum, SEA of silver ammine is demonstrated to be a simple, reproducible way to synthesize small particles on all supports but carbon.

Keywords: Strong electrostatic adsorption; Ag catalysts; Silver diammine; Silica; Alumina; Zirconia; Niobia; Carbon.

Introduction

Supported silver nanoparticles are catalytically active for a variety of chemical reactions, including decomposition of ozone[1], reduction of NO_x [2,3], epoxidation of alkenes[4,5], dehydrogenation of alcohols[6-9], and reduction of nitrophenols[10,11]. Some of these reactions require relatively large Ag particles, but some (i.e., dehydrogenation of alcohols and selective catalytic reduction of NO_x) proceed with higher rates over supported Ag nanoparticles with relatively small dimensions, suggesting that the architecture of supported Ag particles must be strictly controlled for each individual chemical process.

Extensive efforts have been made to synthesize supported silver nanoparticles with desired dimensions and shapes. Table S1 provides a short literature survey of selected properties of Al_2O_3 - and SiO_2 -supported Ag samples prepared by incipient wetness (IW), wet impregnation (WI), and sol-gel methods. While this survey is not exhaustive, a number of trends affecting the size of Ag particles in these materials can be identified. For example, AgNO_3 is used most frequently as a precursor for all these conventional preparations techniques and high temperature treatments are employed to form metal particles. The support nature appears to be a crucial factor, as average dimensions of silver particles formed on Al_2O_3 and SiO_2 supports were found to be on the order of 11 and 3 nm, respectively[12,13]. For each specific support, calcination in air at approximately 500°C typically leads to a higher metal dispersion as compared to the case when the calcination step is followed by reduction in H_2 at elevated temperatures[14]. In the latter case, however, the size of Ag particles increases with reduction temperature. For example, in the case of 8% Ag/SiO_2 prepared by IW and calcined at 500°C , average sizes of Ag particles were found to be 4.5 and 16.7 nm after reduction with H_2 at 200 and 500°C , respectively[15]. Finally, Table S1 also shows that when AgNO_3 was used to prepare silver nanoparticles in solution and Ag colloids thus formed were further used to prepare solid catalytic materials, large Ag particles with sizes on the order of 150-220 nm were formed regardless of the support nature and activation conditions used[16]. Overall, these literature examples clearly show that conventional preparations techniques based on the impregnation of Ag salts and high temperature treatments provide only a limited control over Ag particle sizes in solid materials because Ag easily aggregates at elevated temperatures.

Some literature reports also describe the synthesis of Ag/SiO₂ from AgNO₃ using a modified IW impregnation method in which the pH of the initial AgNO₃ aqueous solution was adjusted to 11 with ammonium hydroxide. When 2% Ag/SiO₂ prepared in this way was calcined in air at 500°C, the following reduction treatment in H₂ at 200°C for 2 h yielded Ag nanoparticles on the SiO₂ surface with an average size of approximately 0.8 nm [17]. While pH adjustments were used in this case mainly to improve the interaction between Ag species and the support surface during the impregnation step, one cannot ignore the formation of Ag(NH₃)₂⁺ complexes in solution under reported conditions.

Only few other reports, demonstrating the formation of supported silver nanostructures from diammine complexes, Ag(NH₃)₂⁺, can be found to date [18-20]. For example, it has been shown that the treatment of SBA-15-supported Ag(NH₃)₂⁺ complexes in O₂ at 300°C followed by reduction with H₂ at the same temperature leads to the formation of relatively small (4 nm) Ag nanoparticles or long (50 nm) Ag nanowires, depending on the Ag loading used [18]. The formation of Ag nanoparticle “necklaces” has been observed upon treatment of colloidal silica with Ag(NH₃)₂⁺ solution followed by washing and ageing [19]. When Ag colloids prepared via chemical reduction of Ag(NH₃)₂⁺ by formaldehyde were used to fabricate Ag/SiO₂, it was possible to control sizes of supported Ag nanoparticles in the 2-10 nm range using a chemical etching method [20].

In addition to the synthesis of various supported Ag structures, several literature reports illustrate the beneficial catalytic properties of nano-sized particles. For example, it has been shown that Ag⁺-exchanged zeolites are capable of activating CH₄ and, therefore, catalyzing the reaction of CH₄ and C₂H₄ coupling to form propene [21]. Hydrotalcite-supported Ag particles with an average diameter of 3.3 nm were found to be active for dehydrogenation of alcohols [22]. It has been shown that Ag₃ clusters deposited from a molecular beam on amorphous alumina films and 3.5 nm Ag nanoparticles formed from them at elevated temperatures can catalyze propene epoxidation with the latter species being more selective toward propylene oxide at temperatures up to 120°C [23]. Finally, unique catalytic properties of subnano- and nano-sized Al₂O₃-supported Ag clusters in selective catalytic reduction of NO_x by hydrocarbons and a variety of environmentally friendly organic reactions have been reported elsewhere [24-27].

Although the findings mentioned above indicate that supported Ag nanostructures tend to have higher activities and selectivities for specific reactions, a controllable and repeatable method to synthesize small Ag nanoparticles does not appear to have been demonstrated. The purpose of this paper is to demonstrate that “Strong Electrostatic Adsorption” (SEA)[28-30] is one such method.

SEA exploits the protonation-deprotonation chemistry of oxide and carbon surfaces in solutions. Every oxide support has a point of zero charge (PZC) and by definition, the PZC is the pH at which the support surface is neutrally charged. When the solution pH is below the PZC value, the hydroxyl groups are protonated and become positively charged. Under these conditions, the surface can adsorb anionic metal complexes. The same groups become deprotonated and negatively charged when the solution pH is above the PZC of the oxide support, and thus positively charged species can be adsorbed by the support surface[28,29]. To date, the electrostatic adsorption mechanism has been demonstrated mainly for noble metal complexes, including anionic hexachloroplatinate (and related hydrolysis products) over alumina[31], cationic Pt tetraammines over silica[32-34], cationic and anionic Pt complexes over carbon[35-37].

In this work, the uptake of Ag diammine complexes by supports with low and mid-range PZCs (i.e., Nb₂O₅, SiO₂, Al₂O₃ and ZrO₂) is examined and used to prepare highly dispersed supported Ag nanoparticles. Unlike other ammine complexes, silver exhibits two uptake maxima, the first of which (at the lower pH) appears to involve the additional deposition mechanism of ion exchange near the PZC of some of the materials.

Materials and Methods

Commercial Nb₂O₅ (Companhia Brasileira de Metalurgia e Mineração – CBMM), ZrO₂ (Toyota), γ -Al₂O₃ (Toyota), fumed SiO₂ (Evonik) and oxidized carbon (Asbury) supports with BET surface areas of 186, 96, 167, 148, and 114 m²/g, respectively, were used as supplied. AgNO₃ (99% purity, Aldrich), 1 N NH₄OH (Alfa Aesar), and 5 N NaOH (Alfa Aesar) aqueous solutions were used as received. Deionized water purified to 18.2 M Ω ·cm (Milli-Q grade) was used to prepare all aqueous solutions.

The PZC of each support was determined by the method described elsewhere[38]. In a typical measurement, appropriate amounts of each specific support were added to aqueous solutions adjusted to different initial pH values to achieve a surface loading (the total support area per liter of solution) of 10,000 m²/L. Solutions were allowed to stabilize for approximately 1 h and the pH was measured again. The PZC of the solid corresponds to a plateau on a plot of final pH vs the initial pH[38]. Based on these measurements, Al₂O₃ and ZrO₂ supports were found to have medium PZC values of 7.8 and 6.8, respectively, while SiO₂, Nb₂O₅, and carbon have low PZC values of 4, 3, and 4.7, respectively.

Silver diammine nitrate (Ag(NH₃)₂NO₃), also known as a Tollen's reagent, was prepared according to a two-step procedure reported elsewhere[20]. In short, a 3.15·10³ ppm AgNO₃ aqueous solution was initially prepared by dissolving 0.315 g of AgNO₃ in 100 mL of deionized water. The resulting solution was transferred to a 1 L volumetric flask and 450 µL NaOH solution (5 N) was added drop wise to the flask, leading to the formation of a brown precipitate (Ag₂O).

The subsequent addition of 12 mL NH₄OH (1 N) to the mixture dissolves the precipitate due to the formation of Ag(NH₃)₂⁺ complexes.

The 1 L volumetric flask was filled with deionized water to yield a 200 ppm Ag concentration in the final solution with a basic pH of 11.3. The solution was vigorously stirred during the whole preparation procedure and an amber flask was used due to the light sensitivity of silver.

Approximately 40 mL aliquots of the stock Ag(NH₃)₂NO₃ solution were used to determine the nature of Ag species existing in solution at different pH values. In each case, the pH of the solution was adjusted to a desired value with 1.2 M HNO₃ or 1 M NaOH solutions, as it was appropriate, the acquired solution was stirred until no changes in pH were observed, and examined by UV-vis.

Adsorption experiments were performed at a constant surface loading of 1000 m²/L. In these experiments, appropriate amounts of each support were added into 40 mL aliquots of the stock Ag(NH₃)₂⁺ solutions the pH of which was adjusted in the 1-13 range (pH_{Initial}) with 1.2 M HNO₃ or 1 M NaOH solutions, as appropriate. Suspensions thus formed were vigorously stirred and sampled for pH after 1 h (pH_{Final}). Then, 3-4 mL portions of these suspensions were removed, the solid was filtered, and the liquid phase was analyzed by Atomic Absorption (AA) for the Ag content. The adsorption density of Ag (Γ_{Ag}), expressed as micromoles Ag adsorbed per square meter of the support surface, was calculated as:

$$\Gamma_{Ag} = \frac{(C_{Ag,Initial} - C_{Ag,Final})(\mu\text{mol/L})}{SL (m^2/L)} = \text{uptake } (\mu\text{mol/m}^2)$$

Where $C_{Ag,Initial}$ and $C_{Ag,Final}$ are initial and final concentrations of Ag in solution, respectively, and SL is the surface loading.

A Perkin Elmer (AAnalyst 400) atomic absorption spectrometer was used to quantify the concentration of Ag in solutions. Calibration standards were prepared from a 1000 ppm Ag stock solution (J. T. Baker) and the calibration curve obtained was verified with an independent second standard solution of 2 ppm Ag in 5% (v/v) HNO₃ (Ultra Scientific). All solutions were stored in amber glass volumetric flasks for light protection. Before measurements, all solutions were diluted with 5% HNO₃ to reach the 0-5 mg/L range of Ag concentrations.

UV-vis spectra were collected at room temperature using a Shimadzu UV-2010PC spectrophotometer and quartz cells with a path length of 10 mm. All samples were scanned in the 190–800 nm range at 0.5 nm steps. Deionized water was used as the reference for all measurements.

To synthesize catalytic materials in sufficient quantities, the adsorption experiments were simply scaled up as has been previously reported [37,39]. Approximately 1 g of each specific support was mixed with an appropriate amount of a 200 ppm Ag(NH₃)₂⁺ stock solution the pH of which was adjusted to a desired value to yield a suspension with surface loading of 1000 m²/L. The suspension was stirred for 1 h before the solid was separated by filtration and dried at room temperature for 48 h. The elemental analysis of solutions before and after interaction with the support was used to determine the Ag loadings in solid materials. Solid samples thus formed

were treated with a 10% H₂/He mixture while the temperature was ramped at 2°C/min to 100°C and held at this temperature for 2 h; TPR profiles (not shown) confirmed the reduction of Ag.

Powder X-ray diffraction (XRD) measurements were performed using a Rigaku MiniFlex II bench top system with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 30 kV and 15 mA. This instrument features a high sensitivity solid state (D/tex Ultra) detector with a detection size limit of about 1.5 nm. Scans were made in the 10°-70° 2 θ range, with a step size of 0.02°, and a scan rate of 0.5°/min. The XRD particle size was calculated using the Scherrer equation with a shape factor of 0.94.

BET surface area measurements and TPR were performed using a ChemBET-3000 analyzer (Quantachrome Instruments). All supports were outgassed in He at 120°C for 3 h prior to measurements. The surface area of each support was then determined by N₂ adsorption using a multipoint BET method.

Results and Discussion

Ag Solution Stability and Speciation

The stability of the 200 ppm Ag diammine solution at different pH values was examined first and results obtained are shown in Fig. 1, where the concentration of Ag (determined by AA) for replicated sets of solutions aged for 1 h is plotted as a function of the solution pH. The data of Fig. 1 clearly show that the concentration of Ag remains nearly unchanged in solution when 1.2 M HNO₃ in appropriate amounts was used to adjust pH values in the 3-11 range, suggesting that this range of pH is the most suitable for SEA measurements. In contrast, when 1 M NaOH was used to cover the range of pH values above 11.3, the concentration of Ag in solution sharply declined. This result was expected, as Ag(NH₃)₂⁺ complexes are not stable in strongly basic solutions and their decomposition leads to the formation of insoluble Ag₂O [40].

At the low end of the pH scale, Ag(NH₃)₂⁺ can undergo ligand exchange to yield Ag(H₂O)₂⁺ aquo complexes [41] according to:

To study the speciation of Ag at lower pH values, UV-vis spectroscopy was used. Fig. 2 shows UV-vis spectra of $\text{Ag}(\text{H}_2\text{O})_2^+$ and $\text{Ag}(\text{NH}_3)_2^+$ aqueous solutions containing 1500 ppm of Ag. This relatively high concentration of Ag was chosen to obtain spectra with a reasonable intensity of absorption bands. The UV-vis spectrum of $\text{Ag}(\text{H}_2\text{O})_2^+$ aquo complexes (Fig. 2A, spectrum 1) is characterized by a single relatively strong absorption band at 300 nm, while the spectrum collected for the aqueous solution of $\text{Ag}(\text{NH}_3)_2^+$ (Fig. 2A, spectrum 2) features a weaker absorption band at approximately 400 nm [42,43]. Since these bands are well resolved, it is possible to estimate the speciation of Ag in the solution during conversion of $\text{Ag}(\text{NH}_3)_2^+$ to $\text{Ag}(\text{H}_2\text{O})_2^+$ complexes with decreasing the solution pH by monitoring their intensity, as shown in Fig. 2B. The band at 400 nm assigned to $\text{Ag}(\text{NH}_3)_2^+$ continuously declines in intensity as pH lowers, while a new band simultaneously develops at 300 nm and increases in intensity, signifying transformation of $\text{Ag}(\text{NH}_3)_2^+$ into $\text{Ag}(\text{H}_2\text{O})_2^+$ complexes (reaction 4). When the results of the UV-vis experiments are quantified as shown in Fig. 3, it becomes evident that $\text{Ag}(\text{H}_2\text{O})_2^+$ aquo complexes dominate in solution at pH values below 9.3, while Ag amines are the dominant species in more basic solutions. However, there is a relatively wide range of pH values (approximately 8.3-10.3) when both types of Ag species coexist in solution in various concentrations. The formation constant (K_f) of $\text{Ag}(\text{NH}_3)_2^+$ species from $\text{Ag}(\text{H}_2\text{O})_2^+$ in water ($\text{Ag}(\text{H}_2\text{O})_2^+ + 2\text{NH}_3 \leftrightarrow \text{Ag}(\text{NH}_3)_2^+ + 2\text{H}_2\text{O}$) at 25 °C is $1.7 \cdot 10^7$ [44] and equilibrium speciation computed based on this constant is reasonably consistent with the experimental data in Fig. 3.

Silver uptake surveys

The uptakes of silver as a function of pH_{Final} and the corresponding shifts in pH values over all examined materials are shown in Fig. 4. Two trends are observed in the uptake surveys (left hand side graphs). First, the maximum Ag uptake increases as the PZC drops, and second, for all supports (except silica), two maxima appear in the Ag uptake profiles. The pH shifts for the metal-free control and metal-containing experiments (right hand side graphs) also exhibit two trends. First, in the high pH region, the pH values of the metal containing solutions are above those of the control experiments, indicating the consumption of protons during adsorption. The

consumption of protons is caused by the speciation of $\text{Ag}(\text{NH}_3)_2^+$ complexes, as the ammine ligands (NH_3) released from the metal complex are converted into ammonium ions (NH_4^+) (reaction 4). This process is nearly complete at a pH of approximately 6 (Fig. 3). Speciation-driven proton consumption is especially evident in Fig. 4J, where larger pH shifts are observed for the higher metal concentration. Second, for the alumina, zirconia, and niobia cases, the pH of the metal containing solutions falls below the control experiment at low pH, indicating the generation of protons during metal deposition.

The maximum uptake of cationic precursors via electrostatic adsorption is expected to increase with lower PZC materials [39,46-49] and this can explain the higher surface densities of the high-pH maxima as substrate PZC drops (left hand side graphs of Fig.4). The surface densities observed for all supports except niobia (i.e., in the range from $0.4 \mu\text{mol}/\text{m}^2$ for alumina to $1.6 \mu\text{mol}/\text{m}^2$ for silica) are typical of cationic metal complexes retaining two or one hydration sheath [50,51]. The diameter of $\text{Ag}(\text{NH}_3)_2^+$ is $3.93 \text{ \AA}$ [51,52], such that the area of a hydrated ($d_{\text{H}_2\text{O}} = 2.75 \text{ \AA}$) silver ammine complex is $\pi(3.93/2 + 2.75)^2 = 70. \text{ \AA}^2/\text{complex}$, which converts to $2.4 \mu\text{mol}/\text{m}^2$. By the same calculation, if the diammine complex retains two hydration sheaths, the maximum density would be $0.95 \mu\text{mol}/\text{m}^2$. It would then appear that the diammine complexes retain an average of between one or two sheaths. Surface densities over silica approaching this value have been seen with $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ [53,54].

A notable result over niobia is the complete uptake of the 200 ppm solution over a very wide pH range; the niobia surface could only be saturated with a 1500 ppm solution (Fig.4I). The maximum level of uptake over niobia was as high as $14 \mu\text{mol}/\text{m}^2$. High metal ammine uptakes over niobia have been observed in the past with platinum amines [55]. Niobia contains more than $12 \text{ OH}/\text{nm}^2$ [56] on its surface, that is much more than that of alumina ($8 \text{ OH}/\text{nm}^2$) and silica ($5 \text{ OH}/\text{nm}^2$) [9,32]. The significantly higher hydroxyl density of niobia may impart to the deprotonated surface sufficient coulombic attraction to overcome the solvation energy of removing the hydration sheaths of the adsorbing complex. Calculated as unhydrated disks of radius $3.93 \text{ \AA}$, the uptake of Ag ammine complexes would be $\pi(3.93)^2 = 12 \text{ \AA}^2/\text{complex}$, which converts to $8.3 \mu\text{mol}/\text{m}^2$. This is not too far from the observed maximum value of about $14 \mu\text{mol}/\text{m}^2$, especially if it is considered that the linear, rod-shaped diammine complexes would pack more densely than disks on which the calculation is based. The dip in Ag uptake after the

first maximum at pH 7 can be explained by the transition of uptake mechanism from ion exchange to electrostatic adsorption; as pH increases the neutral surface becomes more negatively charged, as the $\text{Ag}(\text{OH})_2^+$ species are converted to $\text{Ag}(\text{NH}_3)_2^+$ species as. Deposition by ion exchange of $\text{Ag}(\text{OH})_2^+$ over the $-\text{OH}$ groups is apparently not compensated by electrostatic adsorption of the diammine complexes until the pH is significantly above the PZC of the niobia surface.

Silica (Fig. 4G and H) exhibits neither a low pH maximum, nor a low pH production of protons, implying that silver species do not ion exchange over silica. The maximum uptake of $1.6 \mu\text{mol}/\text{m}^2$ (Figure 4G) it is consistent with other metals adsorbing with one hydration sheath on silica [33]. On the other hand, protons are also not released over carbon (Figs. 4E and F), and the Ag uptake occurs over a very wide pH range. This can be attributed to the reactivity of the silver complex to carbon, for which, in fact, Tollen's reagent is known [57]. Specifically, the carbon uptake curve has two maxima at pH 8 and 11.8, where the majority of the Ag species are $\text{Ag}(\text{H}_2\text{O})_2^+$ and $\text{Ag}(\text{NH}_3)_2^+$, respectively (Fig. 3). This indicates that depending on the adsorption pH carbon is reactive towards different Ag species. In summary, it appears that the deposition of silver over carbon is purely reactive, over silica purely electrostatic, and over alumina, zirconia, and niobia involves ion exchange near the PZC of these oxides and electrostatic at higher pH values.

In the absence of ammonia, $\text{Ag}(\text{H}_2\text{O})_2^+$ can precipitate at high pH leading to the formation of Ag_2O . Figs. 5A and 5B show a comparison between $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Ag}(\text{H}_2\text{O})_2^+$ adsorption over silica and niobia supports, respectively. To prevent immediate precipitation of $\text{Ag}(\text{H}_2\text{O})_2^+$ in generating its uptake curve the supports were added into the AgNO_3 aqueous solution at a pH of approximately 6.0 and the pH was adjusted upward with appropriate amounts of NaOH. In this manner, typical of deposition-precipitation[50], the precipitation of $\text{Ag}(\text{H}_2\text{O})_2^+$ is induced over the support surfaces. The Ag uptake curves obtained with the AgNO_3 aqueous solution for these low PZC supports, silica in Fig. 5A and niobia in Fig. 5B, are similar. In both cases, the deposition of $\text{Ag}(\text{H}_2\text{O})_2^+$ is most likely electrostatic at pH 6 and below, as $\text{Ag}(\text{H}_2\text{O})_2^+$ does not precipitate in this pH region. However, precipitation of $\text{Ag}(\text{H}_2\text{O})_2^+$ takes place at pH higher than 6 and this deposition mode supplements the SEA in some range of pH values but most likely prevails as the solution becomes increasingly basic. The Ag uptake curves reach

maxima at a pH of approximately 9.5 and 7.5 for silica and niobia, respectively, and remain unchanged thereafter, consistent with a complete precipitation of $\text{Ag}(\text{H}_2\text{O})_2^+$ (surface or otherwise) under these conditions. The particle sizes resulting from these two deposition regimes, surface precipitation of $\text{Ag}(\text{H}_2\text{O})_2^+$ at high pH and SEA of $\text{Ag}(\text{NH}_3)_2^+$, are reported in the next section.

Synthesis of Ag nanoparticles

In order to synthesize the amount of catalyst needed for the XRD characterization, the adsorption survey experiments were simply scaled up to 1.0 L of solution. Adsorption of $\text{Ag}(\text{NH}_3)_2^+$ was performed at pH values where the two Ag adsorption maxima were observed (Fig. 4, corresponding to ion exchange and electrostatic uptake), and deposition of $\text{Ag}(\text{H}_2\text{O})_2^+$ was conducted at a lower pH corresponding to electrostatic adsorption and a higher pH of precipitation (Fig. 5). The XRD patterns of Ag nanoparticles prepared from $\text{Ag}(\text{NH}_3)_2^+$ versus $\text{Ag}(\text{H}_2\text{O})_2^+$ are shown in Figure 6 on the left and right hand sides, respectively, and the XRD particle sizes are summarized in Table 1. The deposition of Ag amines from a 200 ppm solution over silica at intermediate (8.3) and optimal (9.9) pH levels (Fig. 6a) yields samples with Ag loadings of 1.7 and 2.5 wt.%, respectively. After reduction these samples exhibit no crystallinity in XRD, consistent with the formation of ultra-small Ag nanoparticles below the limit of XRD detection (about 1.5 nm). With 200 ppm Ag aquo complexes, no Ag crystallites were observed at the intermediate pH of 8.3 (Fig. 6b) but at pH 10.5, the resulting Ag particles were on the order of 17 nm.

Over niobia, two Ag diammine uptake maxima were observed at pH 7.8 and 11.5 (Fig. 4I) and Ag loadings of Ag/ Nb_2O_5 prepared at these pH values were found to be 14 and 15 wt.%, respectively. Broad XRD peaks were observed that correspond to Ag particles of approximately 3.5 nm in size (Fig. 6c). The relatively low area of these peaks relative to the 15 wt% sample in Figure 6d suggests that further fractions of the ammine-derived samples exist as particles below the limit of XRD detection. XRD patterns of samples prepared from 200 ppm Ag aquo complex solutions at pH 5.25, where the aquo and ammine complexes show the same uptake (Fig. 5b), and pH 9, where the aquo uptake is much higher than the ammine, are shown in Fig. 6d. In both cases, Ag peaks are sharpened and of higher overall intensity than the peaks of the Ag ammine

precursors in Figure 6c. The pH 5.25 pattern was deconvoluted into two peaks of 20 and 3.4 nm, for an overall weighted average size of 3.9 nm, while the pH 9 sample is comprised of 2.7 and 12 nm peaks for an overall average of 4.9 nm.

On carbon, XRD-patterns shown in Figs. 5e and f for the ammine and aquo complexes respectively include sharp Ag metal peaks and the determined Ag particle sizes are on the order of 20 nm, regardless of the pH and the precursor used. This is consistent with the reactive deposition mechanism of silver over carbon. It appears that the aquo complexes react in a fashion similar to the ammine, even though the lower XRD peak intensity of Ag/C prepared from Ag diammine at pH 11.7 (Fig. 6e, upper pattern) suggests that at least some of the Ag particles are below the XRD detection limit; there may be an electrostatic component to a predominantly reactive deposition for the ammine precursor.

For the sake of comparison, two other Ag nanoparticles synthesis methods— thermal spreading of Ag₂O and incipient wetness impregnation – were explored and are detailed in the supplementary information. Thermal spreading was explored in light of literature reports on the ability to disperse Ag onto supports by calcination over alumina [26] and silica [20]. Briefly, it was found that Ag can be induced to wet the surfaces of alumina and niobia to a limited extent, but not silica or zirconia. Second, incipient wetness impregnation (IW) was conducted with Ag ammine at weight loadings corresponding to the SEA experiments. Large particles appeared on niobia and alumina, and these could be reduced in size by calcination as seen in the thermal wetting experiments, and particles over carbon were again large. Smaller particles formed over silica and zirconia as determined by XRD, but upon closer inspection with electron microscopy, small numbers of very large particles did appear over silica.

Conclusions

Silver diammine complexes are converted to Ag(H₂O)₂⁺ aquo complexes below pH 11 and hydrolyze to insoluble Ag₂O above pH 11. Deposition of either Ag complexes over carbon at any pH appears to be reactive, resulting in large (~20 nm) metal particles. The Ag(H₂O)₂⁺ aquo complexes appear to adsorb via ion exchange near the PZC of alumina, zirconia, and niobia but not silica, but precipitates to form large particles at high pH, while the Ag(NH₃)₂⁺ complexes appear to adsorb electrostatically at high pH over all the oxides tested - niobia, silica, zirconia, and alumina. Niobia is able to adsorb the maximum amount of silver via both

mechanisms. The particles obtained via electrostatic adsorption at high pH appear to be somewhat smaller than $\text{Ag}(\text{H}_2\text{O})_2^+$ ion exchanged at the lower pH values. SEA with Ag diammines at high pH is demonstrated to be a simple, reliable method to synthesize small Ag nanoparticles over all oxide supports, but reacts to form large particles on carbon.

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Fig. 1. Concentration of Ag in an aqueous silver diamine solution as a function of pH.

Fig. 2. UV-vis spectra of (A) 1500 ppm aqueous solutions of $\text{Ag}(\text{H}_2\text{O})_2^+$ (1) and $\text{Ag}(\text{NH}_3)_2^+$ (2) and (B) 1500 ppm aqueous solution of $\text{Ag}(\text{NH}_3)_2^+$ at pH (1) 11.3, (2) 9.3, and (3) 8.3.

Fig. 3. Experimental mole fractions of $\text{Ag}(\text{H}_2\text{O})_2^+$ (1) and $\text{Ag}(\text{NH}_3)_2^+$ (2) species calculated from UV-vis data and theoretical $\text{Ag}(\text{H}_2\text{O})_2^+$ and $\text{Ag}(\text{NH}_3)_2^+$ mole fractions (3) - calculated by using the $\text{Ag}(\text{NH}_3)_2^+$ species formation equilibrium: $\text{Ag}(\text{H}_2\text{O})_2^+ + 2 \text{NH}_3 \leftrightarrow \text{Ag}(\text{NH}_3)_2^+ + 2 \text{H}_2\text{O}$ ($K_f = 1.7 \cdot 10^7$ [39]) and the $\text{NH}_3/\text{NH}_4^+$ equilibrium ($K_b = 1.8 \cdot 10^{-5}$ - as a function of the solution pH .

Fig. 4. Ag uptakes for a 200 ppm silver diamine solution as a function of pH and corresponding pH shifts observed over alumina (A and B), zirconia (C and D), oxidized carbon (E and F), silica (G and H), and niobia (I and J), respectively. In all cases, the surface loading is 1000 m^2/L .

Fig. 5. Comparison of Ag uptakes from 1500 ppm $\text{Ag}(\text{H}_2\text{O})_2^+$ and $\text{Ag}(\text{NH}_3)_2^+$ solutions by silica (A) and niobia (B) as a function of final pH (In all cases, the surface loading is $1000 \text{ m}^2/\text{L}$).

Fig. 6. XRD patterns of solid samples prepared over silica (a and b), niobia (c and d), and carbon (e and f)

f) from Ag diamine or Ag aquo complexes solutions, respectively.