Mechanistic Elucidation of the Structure and Reactivity of Bare and Hydride-Protected Ag⁺₁₇ Clusters

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Supporting Information

ABSTRACT: We report an approach to create bare silver cluster Ag₁₇⁺ and hydride-rich Ag₁₇H⁺₁₄ separately, as pure species uncontaminated with other entities, in the gas phase starting from a solution-phase monolayer-protected cluster, $Ag_{18}H_{16}(PPh_3)_{10}^{2+}$. These clusters can be synthesized just by applying a small potential on the cone of the mass spectrometer, during electrospray mass spectral analysis. Both the clusters were trapped and reacted with reactive gases like carbon monoxide and acetylene. Unusual products like $Ag_{17}(CO)_7^+$ were observed when Ag₁₇⁺ was reacted with CO in the trap. No intermediate species were found. Transfer of H from acetylene to the cluster during reaction was observed, which later reduced acetylene. All of the structures formed were calculated using density functional theory and show interesting facts about the composition of the products and the mechanism of their formation. Most of the structures were observed for the first time.

Ag₁ Ag₁₇(CO)₇ CO in Trap CO in Trap No Reaction

1. INTRODUCTION

Atomically precise monolayer-protected clusters is a rapidly growing area of research in the recent past.¹ Mass spectrometry has been used extensively as a characterization tool for the understanding of these types of clusters, which mostly show a single peak in their soft ionization mass spectra. Unprotected gas-phase clusters² produced in situ belong to a thoroughly researched subject area, and many such species were identified decades ago.^{3,4} In most of the cases, clusters were produced by magnetron sputtering,⁵ fast atom bombardment,⁶ laser ablation,⁷ etc., from metal salts in vacuum⁸ or under ambient conditions⁹ and were identified by mass spectrometry. Theoretical calculations on the structure and reactivity of such clusters have been important to understand their science in greater detail.¹⁰ Numerous metallic,^{10,11} semiconducting,¹² and other¹³ clusters were created so far using these methods, and their unique and interesting properties and structural studies have expanded the field further as the scientific quest evolved. With the advancement in synthetic methods and mass spectrometric techniques, almost any metal or semiconductor cluster could be synthesized in the gas phase. The main drawback of such clusters lies in their broad size distribution and postsynthesis mass selection.^{3,14} Although numerous attempts were made to create single-cluster ions in the gas phase, successes have been limited. Maximum number of studies were focused on catalytic activity of size-selected clusters.¹⁴ Increased number of surface atoms may help in their high catalytic activity.^{15,16}

In contrast, atomically precise monolayer-protected clusters are prepared in solution and their ions are detected in gas phase by mass spectrometry. Gas-phase reactivity study of this class of clusters is still limited as their surface is protected. One way to remove part of the protection is by partial fragmentation of such cluster ions. Collision-induced dissociation (CID) of such clusters results in smaller thiolate fragments, but they never result in intact bare clusters.¹⁷

Gas-phase silver clusters have been reported to show high reactivity and catalytic activity toward carbon monoxide oxidation where silver clusters with different atomicities have been used.^{18–20} Other reactions include O_2 adsorption,¹ propene oxidation,¹⁶ acetylene and ethylene hydrogenation,²¹ reactivity with chlorine,²² reactivity with ethanethiol,²³ NO activation,²⁴ C-H and C-I activation,²⁵ oxygen reduction reaction,²⁶ reactivity toward ammonia,²⁷ selective activation²⁸ etc., to name a few. Supported silver clusters were used for photocatalysis,²⁹ selective hydrogenation,²¹ hydrogen evolution,³⁰ dye degradation,³⁰ catalytic reduction,³¹ dissociation of N_2O ³² etc. The surface oxidation tendency of such gas-phase clusters is very high,³³ and hence they have limited applications under ambient conditions.

A recent report on hydride-rich phosphine-protected silver clusters³⁴ shows a new possibility of creating bare cluster ions



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Source condition optimization to get different clusters CV = Cone Voltage, $\bigcirc = PPh_3$, $\bigcirc = Ag_{17}$, $\odot = H$

Figure 1. Schematic representation of the experimental process. Ions are generated by modifying parameters of the source. The desired ions are then mass-selected and allowed to react with reactive gases, and the products were analyzed. A generalized mass spectrometer setup is shown for clarity. Schematic of the complete instrument is shown in Figure S1.

in the gas phase as hydride ligands can be stripped off by collision-induced dissociation (CID). We had demonstrated a method of synthesis of a single gas-phase species Ag_{17}^+ starting from a precursor $[Ag_{18}H_{16}(PPh_3)_{10}]^{2+}$ in recent reports.^{35,36} The precursor cluster $[Ag_{18}H_{16}(PPh_3)_{10}]^{2+}$ was synthesized using an established procedure reported elsewhere.³⁴ Phosphine ligands were removed following in-source fragmentation by applying a higher cone (extraction) voltage, which resulted in $Ag_{17}H_{14}^+$ clusters. Hydride protection was further removed by applying higher potential, and a pure Ag_{17}^+ cluster was produced. This cluster Ag_{17}^+ is an example of a single gas-phase cluster species produced in one step, synthesized from a different solution-phase precursor.

In the present report, Ag_{17}^{+} has been trapped and allowed to react with carbon monoxide and acetylene. Surprisingly, $Ag_{17}H_{14}^{+}$ did not show any reactivity with CO, implying that the smallest possible ligand, namely, hydride was enough to passivate the reactive cluster surface toward reaction with CO. On the other hand, H exchange occurs when the cluster was reacted with acetylene. Unusual reactivity of the ions with these gas molecules was further studied using density functional theory (DFT) calculations. Theoretical studies show that specific structural sites are responsible for such an activity. All of the geometries discussed in this report were studied theoretically, and the results are in agreement with experiment.

2. EXPERIMENTAL SECTION

2.1. Synthesis of [Ag_{18}H_{16}(PPh_3)_{10}]^{2+}. The cluster was synthesized following a recently reported method by Bootharaju et al.³⁴ In a typical synthesis, 20 mg of AgNO₃ in 5 mL of MeOH was mixed with 100 mg of TPP in 7 mL of DCM and stirred for 20 min. To the colorless mixture, 1 mL of icecold NaBH₄ (35 mg) was added and the color of the solution turned yellow immediately. The stirring was continued for another 10 h in the dark to get a green solution indicating the successful transformation of the reactant to cluster. The assynthesized cluster was rotavapored to remove the solvents and washed repeatedly with Milli-Q water to remove excess reactant. Finally, the clusters were extracted in MeOH for further characterization. During the synthesis of $[Ag_{18}D_{16}(PPh_3)_{10}]^{2+}$ cluster, NaBH₄ was replaced with NaBD₄ and a similar process was followed.

2.2. Mass Spectrometric Details. All mass spectral analyses were performed in a Waters Synapt G2Si instrument with electrospray ionization source (ESI) and ion mobility (IM) cell. This instrument is also capable of analyzing samples in matrix-assisted laser desorption ionization and atmospheric pressure chemical ionization mode. The data were analyzed using MassLynx 4.1 software. All of the species were identified in the positive-ion mode. To obtain intact cluster ion, about 100 μ g/mL sample solution was prepared in MeOH and diluted to 10 times before injecting into a mass spectrometer. The capillary voltage was set at 2 kV, and cone voltage and source offset were set to 0 V. For Ag₁₇H₁₄ ion, the cone voltage and source offset were increased to 120 and 100 V, respectively. The cone voltage was further increased to 150 V to remove all of the H from $Ag_{17}H_{14}^+$ to get bare Ag_{17} cluster ion. A constant 400 L/h desolvation gas flow rate was maintained throughout the experiment without any additional cone gas flow. The capillary temperature was fixed at 100 °C, and the desolvation temperature was set at 150 °C. For MS/ MS analysis, the species were trapped and variable collision energy was supplied through high-purity Ar as collision gas (5 mL/min). Ultra-high-purity He was used as curtain gas in IM cell at a flow rate of 100 mL/min. High-purity N₂ was used in the IM cell with a flow rate of 50 mL/min. A bias voltage of 45 V was applied, while the wave velocity and wave height were maintained at 400 m/s and 40 V, respectively. For reactions in trap, Ar gas was replaced with CO and C_2H_2 . The Ar line was removed and attached to the respective gas cylinder, and the flow rates were controlled using the MassLynx software. Typical trap pressures for 2, 5, and 10 mL/min flow rates were 1.3×10^{-2} , 1.84×10^{-2} , and 3.4×10^{-2} mbar, respectively. All of the reactions were performed at room temperature.

2.3. Computational Details. The structures of the complexes of Ag_{17} with hydrogen and CO were optimized using density functional theory with meta-generalized gradient approximation of Tao, Perdew, Staroverov, and Scuseria exchange-correlation functional. All of the structures were calculated as monocations. Silver atoms were treated with LANL2DZ basis set, and 6-31G* was used for the remaining atoms. The geometry optimization was carried out with no geometric constraints. To ensure that the optimized structures correspond to true minimum, vibrational frequencies were calculated for all of the complexes. Imaginary frequencies were not observed for any structure. All of the calculations were

performed using Gaussian 09 software. The binding energies were calculated using the following equation

binding energy =
$$E_{\text{complex}} - [E_{\text{monomer1}} + E_{\text{monomer2}}]$$

where E_{complex} is the energy of $Ag_{17}(CO)_n^+$, E_{monomer1} is the energy of Ag_{17}^+ , and E_{monomer2} is the energy of nCO, n = 1-7. In a similar way, thermal free-energy differences were calculated using the following equation

free energy difference

$$= FE_{complex} - [FE_{monomer1} + FE_{monomer2}]$$

where $\text{FE}_{\text{complex}}$ is the free energy of $\text{Ag}_{17}(\text{CO})_n^+$, $\text{FE}_{\text{monomer1}}$ is the free energy of Ag_{17}^+ , and $\text{FE}_{\text{monomer2}}$ is the free energy of nCO (n = 1-7).

3. RESULTS AND DISCUSSION

3.1. Formation of Ag⁺₁₇ and Ag₁₇H⁺₁₄. Hydride-rich $[Ag_{18}H_{16}(PPh_3)_{10}]^{2+}$ was synthesized following a recent report.³⁴ Cluster synthesis is sensitive to conditions, and it is important to follow these closely. The cluster was purified and dissolved in MeOH and analyzed by electrospray ionization mass spectrometry (ESI MS) in a Waters Synapt G2Si instrument, which is also equipped with ion mobility separation. At a lower spray voltage, an intact cluster was observed with the molecular ion peak at m/z 2290, which is in agreement with the reported one. With increase in cone voltage and tuning of a few other experimental parameters, it was possible to remove all of the phosphine ligands as well as all of the hydrides from the cluster. In this process, one Ag atom was also lost from the parent cluster and it resulted in a bare Ag₁₇⁺ cluster in the gas phase. A schematic of the synthesis process is shown in Figure 1. In the experiments, source parameters were optimized such that only cone voltage and source offset voltages were changed maintaining all other parameters the same throughout the experiments. At lowest voltages (cone voltage and source offset at 0 V), the intact cluster in its 2+ charge state was observed at m/z 2290. A few other smaller peaks were observed at lower m/z, which are due to PPh₃ losses. When the cone voltage and source offset were set at 120 V, all of the PPh₃ ligands were lost along with an Ag from the core. The peak maxima matched with Ag₁₇H⁺₁₄. Some tailing was observed at lower mass, due to a few $\rm H_2$ losses during in-source fragmentation. 35 The peak was compared to $Ag_{17}H_{14}^+$ and $Ag_{17}H_8^+$ to show the H_2 losses. Better optimization of the species to get fewer H₂ losses is possible with fine tuning of the parameters. When the cone voltage was increased to 150 V, all of the H were lost and the peak due to Ag₁₇⁺ appeared, and the isotope distribution fitted exactly with the calculated one. Similar sequential ligand and H₂ losses were observed during multistage tandem mass spectrometry of $[Ag_{x}H_{x-2}L_{6}]^{2+}$ (where x = 9-15).³⁷ Corresponding mass spectra at different cone voltages are shown in Figure 2. Isotope envelope for each peak is expanded and compared to the calculated pattern shown as insets (i)-(iii). Note that this type of bare cluster synthesis is not instrument-specific. A similar observation was made with another mass spectrometer (in ESI or NESI mode) by tuning the source parameters for effective in-source fragmentation.

Collision-induced dissociation of the parent cluster resulted in a similar type of fragmentation and Ag_{17}^+ was formed.³⁵ Further CID on bare Ag_{17}^+ cluster resulted in smaller silver



Figure 2. (A) ESI MS of $[Ag_{18}H_{16}(PPh_3)_{10}]^{2+}$ in positive-ion mode showing a strong signal for 2+ charged species with a few additional PPh₃ losses. Enlarged view of the molecular ion is shown in (i), which matches perfectly with its calculated isotope pattern. (B) With increasing cone voltage, all PPh₃ ligands were lost from the cluster and a strong peak appeared at m/z 1847, which was assigned as $Ag_{17}H_{14}^+$. (C) At the highest cone voltage, all H atoms were also lost and the bare Ag_{17}^+ cluster peak was observed at m/z 1833. Isotope patterns of each peak are shown in insets (ii) and (iii). DFT optimized structures of the clusters, $Ag_{17}H_{14}^+$, and Ag_{17}^+ are shown alongside the peaks. Parameters of the spectrometer are also given.

clusters, as shown in Figure S2A-E. A series of bare Ag clusters were seen with odd-numbered clusters being higher in intensity compared to the even-numbered ones. Although Ag⁺₈ was found at a reasonable intensity, Ag_{10}^+ was completely absent in the current experimental condition. All of the clusters obtained in this process possess only one major peak in their respective ion mobility mass spectra, confirming the presence of only one type of structural isomer in the gas phase (see Figure S2F). Width of the drift time distribution decreased with the core size. Typically gas-phase clusters show different types of isomeric structures. The absence of multiple isomeric species may be due to enhanced stability of one isomer or very fast interconversion among isomers, faster than the mass spectrometric time scale. The resolution of the instrument might also not be enough to separate such isomers. Experimental $^{\text{TWIMS}}\text{CCS}_{N2}$ is shown in Table S1.

The structure of Ag₁₇ was determined based on the previous report.³⁸ One Ag atom is in the core, while other 16 Ag atoms form the shell. Distribution of these 16 silver atoms is such that four Ag atoms form a parallelogram with the Ag-Ag-Ag bond angle ranging between 58 and 62° and Ag–Ag bond lengths ranging between 2.80 and 2.83 Å. The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap (Δ HL) was found to be 0.205 eV for neutral Ag_{17} and 0.260 eV for Ag_{17}^+ . The optimized structure was used for further calculations. Calculations indicate that 16 silver atoms available on the surface of Ag₁₇ can bind with equal number of hydrogen (H), which is one hydrogen to each surface Ag atom. When the same structure was optimized to a local minimum on the potential energy surface, the terminal H ligands change their bonding pattern to bridge between Ag atoms. During the reorganization process, two vicinal H atoms are bonded to each other and evolved as hydrogen molecule. This may be because of crowding of



Figure 3. Formation of $Ag_{17}H_{14}$ from Ag_{17} was calculated by DFT. During calculation, 16 H atoms were added initially to the DFT optimized structure of Ag_{17} . A complete core conversion was observed with 16 H attachment. During optimization, the bonding pattern of H with Ag changes and two of them were released as H_2 to get the final optimized structure of $Ag_{17}H_{14}$. Silver atoms are gray, and hydrogen atoms are green in color.

hydrogens on the surface of Ag₁₇ during reorganization. Now, the cluster has only 14 H on its surface, and the optimized geometry is shown in Figure 3. In the structure of $Ag_{17}H_{14}$, some hydrogens bind through two and three coordinations while one hydrogen is bonded to a single silver atom. We have also found that there are two vacant sites above the plane formed by three silver atoms. Bridging H is known for silver clusters. Zhao et al. calculated structures of small neutral and cationic Ag_nH (n = 1-7) clusters by DFT³⁹ and found that bridged sites are preferred energetically for cationic and neutral silver clusters. The isomeric structures were constructed by changing the position of the hydrogen, which bind via three coordination as mentioned above. Three isomers were optimized for Ag₁₇H₁₄, and they are shown in Figure S3. The structure of Ag₁₇ is slightly distorted after hydrogenation. The bond lengths between silver atoms increase due to the presence of H. Further, two more H were added to the Ag₁₇H₁₄ cluster and optimized to local minimum on the potential energy surface. The structure of Ag₁₇H₁₆ is also stable. Note that with more than 14 H on the surface, the overall structure of the cluster core also changes (see Figure 3). These data indicate that with more H loading, isomeric cores can be created. A similar core conversion was observed with Ru₁₉ cluster anion upon H loading.⁴⁰

3.2. Reactivity of Ag₁₇⁺ with CO. To understand the reactivity of the bare clusters, the instrumental setup was modified. Through the modified channels, reactive gases were leaked in at desired flow rates and allowed to react with the species of interest. We have made arrangements to inlet gases in the trap by replacing argon lines with a gas of our choice. For the first set of experiments, we have checked with the standard calibrant whether there is any mass shift or additional fragmentation when different gases were leaked into trap instead of Ar at the experimental conditions. Even at maximum flow rates used in our experiments, we have not seen any such anomalies. For the first set of experiments, carbon monoxide (CO) was introduced in the trap (see Figures 1 and S1) and the trapped Ag_{17}^+ ions were allowed to react with it and the product was identified by a time-of-flight mass analyzer. All of the experiments were performed in the resolution mode to get

a perfect isotope resolution, and the data are shown in Figure 4. At lower CO gas flow (2 mL/min), no CO added product



Figure 4. Reaction of Ag_{17}^4 with (A) 2 mL/min and (B) 10 mL/min of CO in the trap showing a peak for 7 CO attachment with the cluster. Isotope patterns of both Ag_{17}^4 and $Ag_{17}(CO)_7^4$ match with their calculated isotope patterns. The insets show DFT optimized structures of (i) Ag_{17}^4 and (ii) $Ag_{17}(CO)_7^4$. Parameters of the spectrometer are also given.

was seen. When the gas flow was gradually increased to 5 mL/ min, a new peak appeared at m/z 2030, which is assigned as Ag₁₇(CO)⁺₇. Dependence of the peak on CO flow is shown in Figure S4A. The peak was enhanced in intensity when 10 mL/ min CO flow was maintained. A weak Ag₁₇(CO)⁺₆ was also observed. Surprisingly, lesser number of CO added peaks were not observed in the lower region of the mass spectrum. When the species was allowed to fragment by CID, bare Ag⁺₁₇ was regenerated (see Figure S4B).

To get a clear picture of the fragmentation pattern, the ions were allowed to pass through the ion mobility cell before the TOF analysis. In this condition, we could find fragments of



Figure 5. DFT optimized structure and electrostatic potential surface of Ag_{17}^+ , $Ag_{17}H_{14}^+$, and $Ag_{17}(CO)_{1-7}^+$ showing electron density on atoms. The blue color represents positive potential, and the red color indicates negative potential.

 $Ag_{17}(CO)_{67}^+$, $Ag_{17}(CO)_{57}^+$, $Ag_{17}(CO)_{47}^+$, etc., confirming stepwise fragmentation; however, all of these species were not seen when normal CID was performed confirming lower stability of such species in the experimental conditions (see Figure S4C). We could not increase the trap gas flow beyond 10 mL/min in the current setup; however, we believe that more CO attachment could be possible if the ions are allowed to react at higher partial pressures of the reacting gas. The hydrideprotected $Ag_{17}H_{14}^+$ did not show any CO uptake in similar experimental conditions.

3.3. DFT Calculations. The reactivity of a cluster depends on its HOMO-LUMO gap. The calculated HOMO-LUMO gaps for the bare and hydrogenated silver clusters (Ag₁₇ and $Ag_{17}H_{14}$) are 0.205 and 0.232 eV, respectively, implying that the reactivity of hydrogenated clusters is less compared to that of the bare one. Calculated electrostatic potential surfaces (based on the partial charge distribution) of the cluster ions are presented in Figure 5. The blue color represents positive potential, and the red color corresponds to negative potential. The electrostatic potential around Ag₁₇⁺ is different from that of $Ag_{17}H_{14}^{+}$. Most of the atoms are in highly positive potential in Ag_{17}^+ , whereas the number of such atoms decreased in the case of Ag₁₇H⁺₁₄. The decreased positive potential represents increased electron density on Ag177H14 compared to Ag17. Mulliken charges on each atom for both the structures (Ag₁₇⁺ and $Ag_{17}H_{14}^+$) are tabled in the Supporting Information (see Tables S2 and S3). These charges also show that most of the atoms in $Ag_{17}H_{14}^+$ are with partial negative charge. The negative charge distribution around $Ag_{17}H_{14}^+$ may be the reason for its reduced reactivity toward CO. For structural optimization, a neutral CO molecule was added sequentially. Carbon monoxide can anchor on the silver cluster through terminal and bridge bonding. The CO molecule binds to the silver atoms of Ag₁₇ in two bonding patterns. The terminal bonding of CO is more stable than the bridging one. Hence, CO is made to bind with Ag₁₇ in terminal positions. There are six possible binding sites on Ag₁₇ for one CO molecule. The possible isomeric structures were optimized (see Figure S5) for

neutral Ag₁₇. The most stable isomer with one CO has been used to bind with the second CO molecule. In the case of the second CO also, nine possible isomers were predicted, and the most stable isomer was used for further addition of a third CO (see Figures S6 and S7). Similarly, four CO attachments led to five isomers (see Figure S8). Like that, we have added five, six, and seven CO similarly (Figures S9-S11). It can be observed that the even-numbered CO molecules were added in a symmetric fashion. Among the most stable isomers in all of the cases presented in Figures S5-S11, the lowest-energy structures with CO (1-7) were further optimized with a positive charge (Figure S12). The binding of CO does not bring significant changes in the structure of Ag₁₇⁺. The electrostatic potential surface of each $Ag_{17}(CO)_{0-7}^+$ is shown in Figure 5, and the Mulliken charges for each atom are given in the Supporting Information (Tables S2 and S4-S10). The positive potential decreases in the core of cluster with the increase in CO concentration, which implies that electron density increases with the addition of CO. The free-energy change and binding energy of CO and Ag₁₇⁺ were calculated and are listed in Table 1. The negative sign of the binding energy values shows stability of these compounds. The binding energy increases with the addition of new CO molecule, and it is higher for $Ag_{17}(CO)_7^+$. The CO uptake capacity of silver cluster increased with the increase in the number of CO molecules. Further, the free-energy changes and the binding

Table 1. Calculated Free-Energy Change and Binding Energy with Sequential Addition of CO for Ag_{17}^+

cluster + CO	ΔG (kcal/mol)	binding energy (kcal/mol)
$Ag_{17}(CO)^{+}$	3.61	-4.83
$Ag_{17}(CO)_{2}^{+}$	-0.69	-19.17
$Ag_{17}(CO)_{3}^{+}$	-3.84	-30.73
$Ag_{17}(CO)_{4}^{+}$	-4.95	-41.46
$Ag_{17}(CO)_{5}^{+}$	-15.85	-63.41
$Ag_{17}(CO)_{6}^{+}$	-23.95	-78.51
$Ag_{17}(CO)_{7}^{+}$	-17.89	-81.16

energies for the formation of complexes between CO and both the neutral and positively charged Ag_{17} were calculated and are given in Tables S11 and S12. The negative sign shows the feasibility of formation of those adducts, similar to the trends in binding energies.

3.4. Reaction with Acetylene Molecules. Both Ag_{17}^+ and $Ag_{17}H_{14}^+$ were separately allowed to react with acetylene in the trap. With increasing acetylene flow rate (from 2 mL/min in Figure 6A to 10 mL/min in Figure 6B), Ag_{17}^+ showed a peak at



Figure 6. (A) Reaction of Ag_{17}^{+} with 2 mL/min and (B) 10 mL/min of C_2H_2 in trap. At 10 mL/min C_2H_2 flow rate, a strong peak was observed, which is assigned as $Ag_{17}C_4H_{10}^{+}$. During reaction, H transfer occurs between the cluster and acetylene molecules, and subsequently, acetylene is reduced. (C) Explanation of the mechanism. The structures were optimized with DFT.

m/z 1892 corresponding to C₄H₁₀ addition. The peak also show tailing toward higher mass range depicting more H addition. The peak was compared to the calculated mass spectra of $Ag_{17}C_4H_{10}^+$ and $Ag_{17}C_4H_{16}^+$, confirming that there is more H attachment possible to the cluster. Addition of two molecules of acetylene should increase the mass by m/z 52. However, additional increase in mass was observed (m/z 58), which could be due to the reduction of adsorbed acetylide $(-C_2H)$ to $-C_2H_5$ on the surface of the Ag₁₇⁺ cluster. The other possibility could be that during collision with acetylene, the cluster uptakes a few H from acetylene molecules and reduces acetylene on the cluster surface. The H-deficient acetylene may react with each other and polymerize to oligoacetylene, which was not detected in the positive-ion mode. The next peak appears at another m/z 58 difference (2 \times C₂H₅ = 58, the reaction discussed above), suggesting that initial H transfer may occur on the cluster surface and acetylene binds to it in the Ag−C≡C−H fashion. Assuming that no reduction of acetylene occurs on the surface, there were initially 16 active sites. Two acetylene molecules and 6 H occupy eight sites, and the remaining eight sites are occupied in the consecutive step, in a similar fashion. This could be the reason why more than four acetylene additions were not observed.

The mechanism of acetylene adsorption and subsequent reduction can be explained by the following equations

$$Ag_{17} + nC_2H_2 \rightarrow Ag_{17}H_n(C_2H)_m + (-C_2H)_{n-m}, 4$$

$$Ag_{17}H_n(C_2H)_{n/4} \to Ag_{17}(C_2H_5)_{n/4}$$

For the reaction shown in Figure 6, n = 16, m = 4, the equation may be written as follows

$$\begin{aligned} &Ag_{17} + 16 C_2 H_2 \rightarrow Ag_{17} H_{16} (C_2 H)_4 + (-C_2 H)_{12} \\ &Ag_{17} H_{16} (C_2 H)_4 \rightarrow Ag_{17} (C_2 H_5)_4 \end{aligned}$$

Similar selective catalytic activation of acetylene and its chemisorption on the cluster surface were observed for anionic Au_n^{41} and cationic Co_n clusters.⁴² Although studies of catalytic effect on acetylene hydrogenation are limited for silver clusters, selective hydrogenation occurs on the active sites of Ag-doped Pd nanoparticles.²² But such type of intracluster H transfer to reduce adsorbed acetylene to ethane was not observed before. The structures of the reaction products were calculated by DFT, and a plausible reaction pathway is shown in Figure 6C. Isomeric structures arise due to one and two ethane adsorption on Ag₁₇⁺ surface, shown in Figures S13 and S14. The mechanism of H exchange was further confirmed when Ag₁₇H⁺₁₄ was used as the precursor for the reaction. The product peak was observed at m/z 1897 and assigned as $Ag_{17}C_4H_{15}^+$ (see Figure S15). The experimental isotope distribution matches exactly with the calculated spectrum. Here also, two molecules of acetylenes were attached at a time and H exchange occurs between $Ag_{17}H_{14}^+$ and C_2H_2 . Due to H exchange with the colliding C_2H_2 , initial width of the parent peak changed, and finally, it got returned almost to its original width when the final product was formed. To support the mechanism, $Ag_{17}H_{14}^+$ was replaced with $Ag_{17}D_{14}^+$ (NaBD₄ was used instead of NaBH₄ during initial synthesis in solution). The product intensity was lower in the case of D. The peak was assigned as $Ag_{17}C_4H_4D_{11}^+$. This implies that at least three H/D should be removed from the surface to accommodate two C_2H_2 molecules (see Figure S16). This study also proves the H/D-capturing capacity of bare Ag_{17}^+ cluster, which may be used as a hydrogen storage material for controlled release of H₂ in the gas phase.

4. CONCLUSIONS

The current work demonstrates a strategic method to create atomically precise gas-phase clusters from a different solutionphase entity. Completely bare and hydride-protected silver clusters show very different reactivities toward different reactive gases. While Ag₁₇⁺ shows seven CO attachments, no CO was attached to Ag₁₇H⁺₁₄. The smallest possible ligand like H can also passivate the cluster surface toward CO and make it catalytically inert. This finding is very important in terms of choosing any such cluster system for catalytic studies. Bare cluster was very reactive toward acetylene and showed H exchange with C₂H₂ during reaction. Hydride-protected cluster also showed similar reactions where the number of H exchange was proved by replacing H with D on the cluster surface. All structures were calculated by DFT, which shed light on the stability and reactivity of such clusters. Unusual product composition was also explained by calculations. We believe that this study will help create reactive clusters, which would enhance our understanding of selective catalysis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b09465.

Instrumental details; control experiments; DFT optimized isomeric structures; Mulliken charge distributions (PDF)

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Notes

The authors declare no competing financial interest.

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