Experimental and theoretical studies of ammonia generation: Reactions of H₂ with neutral cobalt nitride clusters

Shi Yin, Yan Xie, and Elliot R. Bernstein

Citation: The Journal of Chemical Physics 137, 124304 (2012); doi: 10.1063/1.4754158
View online: http://dx.doi.org/10.1063/1.4754158
View Table of Contents: http://aip.scitation.org/toc/jcp/137/12
Published by the American Institute of Physics
I. INTRODUCTION

The heterogeneous catalytic synthesis of ammonia from nitrogen and hydrogen is a very important industrial process, and it offers 40% of the ammonia to nourish the current global population.1 The catalytic reaction to produce ammonia has attracted deep interest for over 100 years now. Chemically, ammonia synthesis is through the Haber-Bosch process, in which ammonia is produced by the reaction of nitrogen and hydrogen over an iron catalyst.2, 3 Many promoted catalysts have been introduced as an alternative ammonia catalyst in the last several decades. The large energy and time consumption required for the ammonia synthesis process have stimulated the search for better or more efficient catalysts working at lower temperatures and pressures.4 Recently, clusters have been shown to be good models for active sites of complex solid state catalysts: clusters are readily accessible by theoretical techniques because they are isolated and their properties are localized. Experimentally clusters are easily generated, characterized, detected, and researched. Molecular level mechanisms for condensed phase catalytic reactions can be understood through the study of gas phase model reactions with clusters. For example, some recently reported gas-phase vanadium oxide cluster studies provide insights into vanadium-based oxide catalysts for selective oxidation of propylene and hydrogen sulfide.5-8 Moreover, theoretical calculations can be used to help us in the interpretation of experimental results and the prediction of detailed reaction mechanisms for finite cluster systems.9-17

Experimental and theoretical studies of ammonia generation: Reactions of H2 with neutral cobalt nitride clusters

Shi Yin, Yan Xie, and Elliot R. Bernstein

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA

(Received 3 August 2012; accepted 31 August 2012; published online 24 September 2012)

Ammonia generation through reaction of H2 with neutral cobalt nitride clusters in a fast flow reactor is investigated both experimentally and theoretically. Single photon ionization at 193 nm is used to detect neutral cluster distributions through time-of-flight mass spectrometry. CoN7 clusters are generated through laser ablation of Co foil into N2/He expansion gas. Mass peaks CoN7H2 (m = 6, 10) and CoN8H3 (m = 7, 8, 9) are observed for reactions of H2 with the CoNm clusters. Observation of these products indicates that clusters CoN7 (m = 7, 8, 9) have high reactivity with H2 for ammonia generation. Density functional theory (DFT) calculations are performed to explore the potential energy surface for the reaction CoN7 + 3H2 → CoN7H3, and a barrierless, thermodynamically favorable pathway is obtained. An odd number of hydrogen atoms in CoN7H3 (m = 7, 8, 9) probably come from the hydrogen molecule dissociation on two active cobalt nitride clusters based on the DFT calculations. Both experimental observations and theoretical calculations suggest that hydrogen dissociation on two active cobalt nitride clusters is the key step to form NH3 in a gas phase reaction. A catalytic cycle for ammonia generation from N2 and H2 on a cobalt metal catalyst surface is proposed based on our experimental and theoretical investigations. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4754158]
dependence of the rate constants for dissociative adsorption of the first D₂ molecule to cobalt clusters Coₘ (m = 9-21) was examined over the temperature range of 133-373 K. The rate constants for clusters m = 10-13, 15-17 show no dependence on temperature, indicating that D₂ chemisorption reaction has no activation barrier. The rate constants for Coₙ and Co₁₄ increase at higher temperatures, which suggest the presence of activation barriers (8.8 and 7.8 kJ/mol, respectively). The reactivity of positive cobalt cluster ions Coₘ⁺ (m = 2-22) with H₂ was investigated using a fast flow reactor. The reactivities of larger cationic cobalt clusters with H₂ are similar to the corresponding neutral cobalt clusters: reactivities of Coₙ⁺ (m = 4-9), however, are found to be much higher than their neutral analogs. Apparently, the positive charge dramatically affects the reactivities of these smaller clusters. The kinetic energy dependent cross sections for reactions of Coₘ⁺ (m = 2-16) with D₂ are studied by a guided ion-beam tandem mass spectrometer. The observed products are CoₙD⁺ for all clusters and CoₙD₂⁺ for m = 4, 5, 9-16. The bond energies for Coₙ⁺–D are found to increase generally as the cluster size increases, and the bond energies of Coₙ⁺–D for larger clusters (m ≥ 10) are found to be very close to the value for chemisorption of atomic hydrogen on bulk phase cobalt.

Reactions of cobalt clusters Coₙ with H₂ are widely investigated in the literature, but the reactions of cobalt nitride clusters with H₂ have not been previously studied, although the dissociation of H₂ and formation of N-H bonds on catalysts are important steps for ammonia synthesis. In this report, the reactions of H₂ with cobalt nitride clusters CoₙNₓ in a flow tube reactor are studied by 193 nm single photon ionization (SPI) coupled with time-of-flight mass spectrometer (TOFMS). Products containing an odd number of H atoms (Co₇₋₉NₓH_3) are found on the cluster series Co₇₋₉N_x, which suggests clusters CoₙN (m = 7, 8, 9) have high reactivity for H₂ for ammonia generation. Detailed reaction mechanisms for generation of NH₃ on Co₇₋₉Ni_3 are suggested based on the experimental observations and DFT calculations for the reaction potential energy surfaces (PESs).

II. PROCEDURES

A. Experimental

The experimental setup for laser ablation coupled with a fast flow reactor employed in this work has been described previously in detail. Only a brief outline of the apparatus is given below. CoₙN_x clusters are generated by laser ablation of a cobalt foil target in the presence of 0.5% N₂ mixed in He expansion gas. A 10 Hz, focused, 532 nm Nd³⁺:YAG laser (Nd³⁺:yttrium aluminum garnet) with 7 mJ/pulse energy is used for the laser ablation. The expansion gas is pulsed into the vacuum by a supersonic nozzle (R. M. Jordan, Co.) with a backing pressure of typically 75 psi. Generated cobalt nitride clusters react with H₂ in a fast flow reactor (i.d. 6.3 mm × 76 mm), which is directly coupled to the cluster generation channel (i.d. 1.8 mm × 19 mm). The reactant gases, H₂ seeded in a pure helium with a 20 psi backing pressure, are injected into the reactor by a pulsed General Valve (Parker, Serial 9). Timing between the Jordan valve and the General Valve opening is optimized for the best product yields. The pressure in the fast flow reactor can be estimated as 14 Torr for the reaction and the collision rate between cobalt nitride clusters and helium is estimated ~10⁸ s⁻¹. Reactants and products are thermalized to 300-400 K by collision after the reaction. An electric field is placed downstream of the reactor in order to remove any residual ions from the molecular beam. The beam of neutral reactants and products is skimmed into a differentially pumped chamber and ionized by an unfocused 193 nm laser and detected in a TOFMS. In order to avoid multiphoton ionization of neutral clusters, the 193 nm laser fluence is set to about 80 μJ/cm²/pulse.

B. Calculational

Density functional theory (DFT) methods have been successfully employed to study structures and properties of the cobalt cluster system. In this work, calculations of the structural parameters for neutral CoₙN_x clusters and the reactions of H₂ with these clusters are performed employing DFT as manipulated in the GAUSSIAN 09 program. All the calculations are carried out with Becke’s exchange and Perdew-Wang’s correlation (BPW91) functional coupled with the modified LANL2DZ basis set for cobalt atoms and the standard 6-311+G(d) basis set for nitrogen and hydrogen atoms. The highly spin-polarized 3d4s electrons of cobalt give rise to directional bonding, magnetism, and Jahn-Teller distortions, yielding structures for which the bonding is maximized. Nonetheless, high magnetic moments still remain, coupled ferromagnetically. To obtain a more precise description of CoₙN_x cluster structures, one would need to use a local spin density approximation and the generalized gradient approximation, or a higher level of theory, such as CASSCF/MRCI calculations, which are successfully used to study structures and thermochemistry of iron sulfur clusters.

The structures of CoₙN_x are optimized for different isomers and spin multiplicities. For each cluster, different initial structures are used as input in the optimization procedure. For each structure, spin multiplicities are scanned from low to high until an energy minimum is found. Calculations for the PESs of ammonia formation reaction on Co₇Ni involve geometry optimizations of the reactants, intermediates, transition states, and products. Vibrational frequency calculations are further performed to confirm the global minima ground states and transition states, which have zero and one imaginary frequency, respectively. Additionally, intrinsic reaction coordinate calculations are carried out to determine that an estimated transition state connects two appropriate local minima along the reaction pathway. Binding energies are calculated employing the counter poise approximation for the basis set superposition error correction; these corrections are found to be insignificant at the present level of theory.

III. RESULTS

A. Experimental results

Figure 1(a) presents a typical TOF mass spectrum of neutral Coₙ (m = 1-18) clusters, and Figure 1(b) presents the
TOF mass spectrum of neutral $\text{Co}_m\text{N}_n$ ($m=1-17$, $n=0-4$) clusters ionized by a 193 nm laser. These clusters are generated by laser ablation of pure Co foil into (a) pure He, and (b) 0.5% N$_2$/He expansion gases at 75 psi backing pressure. The peaks marked with a star and triangle symbol are due to carbon and oxygen impurities, respectively.

Mass spectrum generated from the reaction of neutral cobalt nitride clusters $\text{Co}_m\text{N}_n$ ($m=4-10$) with 2% H$_2$ seeded in helium gas in the fast flow reactor are presented in Figure 2(b). By way of comparison, Figure 2(a) shows the TOF mass spectrum for $\text{Co}_m\text{N}_n$ clusters interacting with only He in the reaction cell. With pure He gas added to the reactor cell, all cluster signals decrease in roughly the same proportion due to scattering by the inert gas (Figure 2(a)). When 2% H$_2$/He is added to the fast flow reactor, the intensity of Co$_m$N$_n$ signal decreases nearly to zero, and the products Co$_m$NH$_2$ ($m=6$ and 10) and Co$_m$NH$_3$ ($m=7-9$) are observed. Products Co$_{6,10}$NH$_2$ are generated from the association reactions,

$$\text{Co}_m\text{N} + \text{H}_2 \rightarrow \text{Co}_m\text{NH}_2.$$  

and are stabilized (cooled) by third body (usually He) collisions. The products Co$_{7,9}$NH$_3$, the additional hydrogen atoms to generate NH$_3$ must come from the dissociation of H$_2$ molecules in multiple cluster molecule collision reactions (see Sec. IV). Based on this behavior, these experimental results suggest that clusters Co$_m$N ($m=7,8,9$) have a high reactivity with H$_2$ for ammonia generation. In order to explore and elucidate this interpretation, the reaction energies, mechanisms, and potential energy surfaces for the Co$_7$N + 3/2H$_2$ reaction system are calculated.

Reactions of Co$_m$ clusters with H$_2$ in the flow tube reactor, and reactions with 0.3% ammonia mixed in the helium in expansion gas are also explored and results are displayed in Figures 3 and S1 (of the supplementary material), respectively. The overall rate constant ($k$) of Co$_m$ + H$_2$ reaction in the fast flow reactor can be estimated as previously described,$^{40,43,60}$ by using the equation $k = \ln(I_0/I)/(\rho \times \Delta t)$, in which $I$ and $I_0$ are signal magnitudes of the clusters in the presence and absence of H$_2$ reagent gas, respectively; $\rho$ is the reactant molecular density; $\Delta t$ is the reaction time ($\sim$50 μs) in the fast flow reactor. The lowest $k$(Co$_6$ + H$_2$) and the highest $k$(Co$_{15}$ + H$_2$) values are estimated to be 1.0 × 10$^{-10}$ and 2.3 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. The absolute error in the values of the rate constants is $\sim$50% based on an estimation of $\rho$ and $\Delta t$ in the experiments. The relative rate constants $k_{rel} = [k$(Co$_m$ + H$_2$)$]/[k$(Co$_{15}$ + H$_2$)$]$ that are independent of the $\rho$ and $\Delta t$ values are plotted in Figure 4. The highest reactivity of Co$_m$ is observed for $m=15$, while the reactivity of Co$_6$ can be lower than the highest one by a factor of about 2 (see Figure 4). Products containing an odd number of hydrogen atoms Co$_m$H$_x$ ($x=1,3$) are observed for
reaction of \( \text{Co}_m \) clusters with \( \text{H}_2 \), and only \( \text{NH}_3 \) adsorption products \( \text{Co}_m(\text{NH}_3)_n \) are observed for reactions of \( \text{Co}_m \) with ammonia. Using the same approach, we can determine qualitative rate constants for the \( \text{Co}_m\text{N} \) clusters reacting with \( \text{H}_2 \) in the reaction cell. Assuming approximately second order kinetics, \( k(\text{Co}_{6-10}\text{N} + \text{H}_2) \) values are estimated to be \( 8.4 \times 10^{-9} \), \( 8.4 \times 10^{-9} \), \( 7.8 \times 10^{-9} \), \( 7.7 \times 10^{-9} \), and \( 8.6 \times 10^{-9} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively. Theoretical results can supply more information as discussed in Sec. III B, concerning the mechanisms associated with this chemistry.

### B. Theoretical results

Figure 5 present the lowest energy structures found for \( \text{Co}_{1-7}\text{N} \) clusters. The nitrogen atom, in such structures for the \( \text{Co}_{3-7}\text{N} \) clusters, is bonded to 3Co atoms. The Co-N distance in these clusters is between 1.741 and 1.896 Å, larger than the CoN (1.617 Å) and the Co2N (1.668 Å) distances. The bond lengths of three Co-N bonds in each cluster of \( \text{Co}_{3-6}\text{N} \) are similar (<0.03 Å difference). For \( \text{Co}_7\text{N} \), the bond length of the Co-N bond, with which the N connects with the top Co (1.896 Å), is 0.1 Å larger than the other two Co-N bonds.
In order to study the mechanism for the ammonia formation reaction (H\textsubscript{2} with reactive Co\textsubscript{7-9}N species), DFT calculations are performed for the reaction Co\textsubscript{7}N + \(3/2\)H\textsubscript{2} → Co\textsubscript{7} + NH\textsubscript{3} (\(\Delta H = -0.73\) eV based on DFT calculations), as an example. The PESs and the optimized geometries of the reaction intermediates and transition states calculated by DFT for this reaction are presented in Figure 6. The structures of intermediate and transition states on this surface are also schematically shown. The minima connected by a given transition state are confirmed by intrinsic reaction coordinate calculations as manipulated in the GAUSSIAN 09 program. The related possible reaction energies of Reactions (2) and (3) are also calculated by DFT,

\[
\text{Co}_7\text{N} + \text{H}_2 \rightarrow \text{Co}_7\text{NH} + \text{H} \quad (\Delta E = 1.27 \text{ eV}),
\]

(2)

\[
2\text{Co}_7\text{N} + \text{H}_2 \rightarrow 2\text{Co}_7\text{NH} \quad (\Delta E = -1.71 \text{ eV}).
\]

(3)

As shown in Figure 6, the first step, formation of Co\textsubscript{7}NH, is taken with a multiple molecular collision Reaction (3). The dissociative adsorption of H\textsubscript{2} on a Co\textsubscript{7}NH cluster to form Co\textsubscript{7}NH\textsubscript{3} (I\textsubscript{2}), is then an exothermic reaction. Every dissociated hydrogen atom of intermediate I\textsubscript{2} is adsorbed by two cobalt atoms, one of which connects with nitrogen. Via transition state TS\textsubscript{1}, one dissociated hydrogen atom transfers to nitrogen from the top cobalt site. The bond length of Cotop-N, connecting the nitrogen atom with the top cobalt, increases to 2.020 Å (compared to the initial bond length 1.896 Å). The other two Co-N bonds length are also increased from 1.787 Å to 1.855 Å, and the –NH moiety is formed (I\textsubscript{3}). The second hydrogen atom transfers to nitrogen via transition state TS\textsubscript{2} to form intermediate I\textsubscript{4}, in which the Cotop-N bond breaks, and the other two Co-N bonds length are increased from 1.855 Å to 1.949 Å. Through transition states TS\textsubscript{3} and TS\textsubscript{4}, the last hydrogen atom transfers to nitrogen and yields intermediate I\textsubscript{6}, for which the formed NH\textsubscript{3} moiety bonds to a Co atom with a 2.067 Å Co-N bond length. A stable intermediate Co\textsubscript{7}(NH\textsubscript{3}) (1.68 eV lower than the initial energy) is formed, and finally generates product Co\textsubscript{7} + NH\textsubscript{3}. Based on DFT calculations, the overall reaction of Co\textsubscript{7}N + \(3/2\)H\textsubscript{2} → Co\textsubscript{7} + NH\textsubscript{3} is barrierless and thermodynamically favorable.
IV. DISCUSSION

A. Reaction of Co\textsubscript{m} clusters with NH\textsubscript{3} and H\textsubscript{2}

Hydrogen chemisorption is one of the best known of all surface chemistries.\textsuperscript{61–64} At room temperature, chemisorption states of H\textsubscript{2} on transition metal surfaces are dissociative, with the two hydrogen atoms well separated at different binding sites on the surface.\textsuperscript{62,65,66} In this work, the reactions of neutral Co\textsubscript{m} clusters with H\textsubscript{2} in the gas phase are studied in a flow tube reactor. The relative rate constants \(k^{\text{rel}}\) shown in Figure 4 indicate that the reactivity of neutral Co\textsubscript{m} clusters with H\textsubscript{2} exhibits a strong size dependence. This observation corresponds well with the size dependence of the Co\textsubscript{m}–D\textsubscript{2} reaction system reported previously.\textsuperscript{31–34}

Figure 3 shows the Co\textsubscript{5} to Co\textsubscript{8} region of the Co\textsubscript{m} mass distribution following Co\textsubscript{m} collision and reaction with pure hydrogen gas. The details of the respective Co\textsubscript{m+8}H\textsubscript{2} distributions are given in the expanded sections of Figure 3. The gaussian fitted peaks are given as the blue and red lines in the expanded sections. As is evident in Figure 3, products containing an odd number of hydrogen atoms are clearly observed. Note that the calculated vertical ionization energies (VIEs) for the lowest energy structures of these observed clusters, such as Co\textsubscript{4}H (5.95 eV) and Co\textsubscript{5}H\textsubscript{2} (6.28 eV), are lower than the 6.4 eV single photon energy of 193 nm radiation. The observation of products containing an odd number of hydrogen atoms is interesting in view of the strength of the H\textsubscript{2} bond: the chemisorption event would have to be incredibly exothermic, releasing more than ~1.8 eV per cobalt-hydrogen bond, in order to enable the ejection of a single H atom into the vacuum, without gaining any other new bonds in the process. For example, hydrogen atom generation is unfavorable for the reaction Co\textsubscript{7} + H\textsubscript{2} \rightarrow Co\textsubscript{5}H + H (\(\Delta E = 1.83\) eV). Thus, an odd number of hydrogen atoms for Co\textsubscript{m+7}H and Co\textsubscript{m+8}H\textsubscript{2} must arise from multiple molecular collision reactions, in which the hydrogen molecule activation reaction occurs for two separate cobalt containing clusters: for example, Co\textsubscript{7} + Co\textsubscript{7} + H\textsubscript{2} \rightarrow Co\textsubscript{7} + Co\textsubscript{7}H\textsubscript{2} \rightarrow 2Co\textsubscript{5}H (\(\Delta E = -0.59\) eV). Multiple molecular collision reactions, generating odd H containing clusters, are also observed in some of our previous studies: for reactions of neutral iron oxide clusters with methanol,\textsuperscript{41} products (CH\textsubscript{2}O)FeOH and FeOH are both observed due to multiple molecule collision reactions (e.g., 2FeO + CH\textsubscript{2}OH); for series reaction products V\textsubscript{m}S\textsubscript{5}C\textsubscript{3}H\textsubscript{3} and V\textsubscript{m}S\textsubscript{5}H\textsubscript{3} observed through multiple molecule collision reactions in the reaction of V\textsubscript{m}S\textsubscript{5} clusters with C\textsubscript{2}H\textsubscript{5} and H\textsubscript{2};\textsuperscript{39} and for reactions forming the cluster systems Mn\textsubscript{m}C\textsubscript{m}H\textsubscript{m} (\(M = Al, Be, Mg\)).\textsuperscript{67,68} These results imply that the multiple molecular collision reactions forming odd H cluster systems are to be expected in the gas phase under typical conditions for the reactions studied.

Finally, only cobalt ammonia association clusters Co\textsubscript{m}(NH\textsubscript{3})\textsubscript{n} are generated by laser ablation of a cobalt foil target in the presence of 0.3% NH\textsubscript{3} mixed in the He expansion gas (see Figure S1 of the supplementary material).\textsuperscript{39} Cobalt ammonia association clusters Co\textsubscript{m}(NH\textsubscript{3})\textsubscript{n} (\(m = 1-8, n = 1-9\)) are observed: Co\textsubscript{5}(NH\textsubscript{3})\textsubscript{n} for \(m = 1-3\), and Co\textsubscript{6}(NH\textsubscript{3})\textsubscript{n-1} for \(m = 4, 5\) are the most intense mass peaks for each series. No dehydrogenated clusters, such as Co\textsubscript{m}N\textsubscript{n}, are detected under these conditions. This result indicates the cobalt ammonia association clusters Co\textsubscript{m}(NH\textsubscript{3})\textsubscript{n} are very stable and that Co\textsubscript{m} will not react with (decompose) NH\textsubscript{3} to generate Co\textsubscript{m}N\textsubscript{n} or Co\textsubscript{m}H\textsubscript{n}.

B. Reaction of Co\textsubscript{m}N clusters with H\textsubscript{2}

Two types of reactions are identified for the interaction of Co\textsubscript{m}N\textsubscript{n} clusters with H\textsubscript{2} in the flow tube reactor experiments presented in Figure 2(b). First, association products Co\textsubscript{m}NH\textsubscript{2} are observed for \(m = 6\) and 10. Second, for \(m = 7-9\), the species Co\textsubscript{m}NH\textsubscript{3} are observed. This size dependent behavior indicates that diverse size dependent reactivities exist for the reaction of Co\textsubscript{m}N\textsubscript{n} clusters with H\textsubscript{2}. The odd number of hydrogen atoms contained in products Co\textsubscript{7}N\textsubscript{n+1} should come from multiple molecular collision reactions, as determined through DFT calculations. Although the calculated VIEs for the lowest energy structures of Co\textsubscript{7}N\textsubscript{2} (5.92 eV) and Co\textsubscript{7}N\textsubscript{3} (5.53 eV) are lower than the 6.4 eV single photon energy of 193 nm radiation, only Co\textsubscript{7}N\textsubscript{3} is observed for reaction of Co\textsubscript{7}N with H\textsubscript{2}: Co\textsubscript{7}NH is not observed. This behavior is different from the reaction of pure cobalt Co\textsubscript{m} clusters with H\textsubscript{2}. For example, products Co\textsubscript{7}H\textsubscript{3} are observed for reaction of Co\textsubscript{7} with H\textsubscript{2} (Figure 3), and mass peak intensities of hydrogen containing clusters decrease with the number of adsorbed hydrogen atoms. This observation indicates that hydrogen adsorption on pure cobalt clusters is controlled by a kinetic process. These results in turn suggest that Co\textsubscript{7}N\textsubscript{3} must be very reactive toward H\textsubscript{2} to form the more stable products Co\textsubscript{7}NH\textsubscript{3}. For \(m = 7-9\), detection of the NH\textsubscript{3} moiety containing products indicates that the barrier for NH\textsubscript{3} moiety formation of intermediate products Co\textsubscript{m}NH\textsubscript{n} must be lower than the initial reactant energy of Co\textsubscript{m}N\textsubscript{n} + 3/2H\textsubscript{2}. In the flow tube reactor, Co\textsubscript{m}N\textsubscript{n} clusters generated from laser ablation are cooled to ~300–400 K due to a large number of collisions with the helium buffer gas. Therefore, if a high barrier exists for the NH\textsubscript{3} moiety formation on Co\textsubscript{7}N\textsubscript{3} clusters, products Co\textsubscript{7}N\textsubscript{2} or Co\textsubscript{7}NH\textsubscript{3} should be observed in the mass spectrum (Figure 2); however, only the products Co\textsubscript{7}N\textsubscript{3} are detected. Thus, Co\textsubscript{7}N\textsubscript{3} (\(m = 7-9\)) is a stable structure, and its formation is controlled by dynamic energetic processes (temperature, barrier, electronic structure, . . . ) rather than by adsorption kinetics.

Instead of NH\textsubscript{3} moiety containing products, only association products Co\textsubscript{6}NH\textsubscript{2} are observed for clusters \(m = 6, 10\). Formation of the NH\textsubscript{3} moiety on cobalt nitride clusters Co\textsubscript{m}N must involve a hydrogen atom transfer from cobalt to the nitrogen atom. From the structures of Co\textsubscript{m}N displayed in Figure 5, the bond lengths of three Co-N bonds in Co\textsubscript{6}N are similar (0.027 Å difference). For Co\textsubscript{7}N, the bond length of Co\textsubscript{opt}-N bond, which connects the N atom with the top Co (1.896 Å), is 0.1 Å larger than that of the other two Co-N bonds, and 0.07 Å larger than the bond length of Co-N bond in Co\textsubscript{9}N. A long bond length for a Co-N connection implies a low barrier for hydrogen atom transfer to nitrogen and initiation of the NH\textsubscript{3} moiety formation process. A similar and shorter bond length for the Co-N bonds in Co\textsubscript{8}N may result
in higher NH₃ formation barriers than the initial energy of Co₆,₁₀N + 3/2H₂; thereby, only H₂/Co₆,₁₀N association products Co₆,₁₀NH₂ are observed in the experiment.

C. Mechanism of ammonia formation on Co₇N cluster and proposed on cobalt metal catalyst surface

The observation of a stable Co₇NH₃ product in the reaction of Co₇N with H₂ suggests that NH₃ can be generated by the reaction Co₇N + 3/2H₂ → Co₇ + NH₃. As the calculation results for the reaction pathways of NH₃ formation on the Co₇N cluster (shown in Figure 6) indicated, the multiple molecular collision reaction is an important step to form a cluster containing an odd number of hydrogen atoms in the reaction. The lowest energy structures of the intermediate I₂ indicate that the activation of the H-H bond on the active Co₇N cluster is a barrierless process, and the dissociated hydrogen connects to or bonds with two cobalt atoms, one of which connects to or bonds with the nitrogen atom. This result suggests that two adjacent Co atoms (one of which connects with nitrogen) of the catalytic Co₇N clusters are the active sites for adsorption and dissociation of the hydrogen molecule in the NH₃ generation reaction. Then the next step in the ammonia formation reaction is the dissociated hydrogen atoms transfer to the N atom to yield the –NH₃ moiety in a stepwise process, and finally generate product Co₇ + NH₃. Free NH₃ molecules cannot be detected by single photon ionization from a 193 nm laser: the ionization energy of NH₃ is ∼10.02 eV. A hot NH₃ scattered out of the molecular beam would not readily transit the skimmer and enter the TOFMS chamber for detection by any ionizing photon.

Catalytic clusters in the gas phase can be seen as a good model system for the active site that exists on a catalyst surface. On a cobalt metal catalyst surface, Co₇-₉N moieties are proposed to be active sites, which have high reactivity with H₂ for ammonia generation, based on our related gas phase studies. The key step for ammonia formation from reaction of neutral Co₇N clusters with H₂ is that an odd number adsorbed hydrogen atoms are generated from multiple molecular collision reactions. Thereby, this model system suggests that ammonia generation from N₂ and H₂ on a cobalt catalyst surface may require two adjacent active sites, and hydrogen atom generation on these two adjacent active sites may be important for the formation of NH₃. Our understanding of a catalytic cycle for ammonia generation on cobalt catalyst surfaces is proposed, and is presented in Figure 7. This proposal is offered based on experimental and calculational results presented in Figures 2 and 6. Dissociation of N₂ is a very difficult step due to the high bond energy for N≡N. Efficient N₂ activation requires more investigation, and should be considered in practical catalysis. H₂ molecules can attach to Co sites, and the activation of the H-H bond is a barrierless process. The dissociated hydrogen atom is attached to two cobalt sites, one of which is connected to a nitrogen atom. Then, the dissociated H atoms can transfer stepwise to the active nitrogen, and the ammonia molecule can be formed and desorbed to the gas phase. Two adjacent active sites may promote hydrogen dissociation, and we suggest that sites, whose structures are like Co₇-₉N, have high reactivity with H₂ for ammonia generation.

V. CONCLUSIONS

Ammonia generation through reaction of H₂ with neutral cobalt nitride clusters in a fast flow reactor is investigated employing TOFMS and 193 nm SPI. Mass peaks CoₘNH₃ (m = 7, 8, 9) are observed for reactions of hydrogen with CoₘNₙ clusters. Theoretical DFT calculations are performed to explore the potential energy surface for the reaction Co₇N + 3/2H₂ → Co₇NH₃, and a barrierless, thermodynamically favorable pathway is obtained. The odd number of hydrogen atoms in CoₘNH₃ (m = 7, 8, 9) clusters probably arise from the hydrogen molecule dissociation reaction on two active cobalt nitride clusters based on the DFT calculations: for example, 2Co₇N + H₂ → 2Co₇NH. Both experimental observations and theoretical calculations suggest that the reaction of ammonia generation requires two active clusters, and hydrogen dissociation on these two active clusters is the key step to form NH₃ in the gas phase reaction. Clusters CoₘN (m = 7, 8, 9) have high reactivity with H₂ for ammonia generation. A catalytic cycle for ammonia generation from
$N_2$ and $H_2$ on a cobalt catalyst surface is proposed based on the present gas phase cluster experimental and theoretical studies.

ACKNOWLEDGMENTS

This work is supported by a grant from the US Air Force Office of Scientific Research (AFOSR) through Grant No. FA9550-10-1-0434, and the National Science Foundation (NSF) through XSEDE resources under Grant No. TG-CHE110083.

45M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 09, Revision A02, Gaussian, Inc., Wallingford, CT, 2009.
54M. Pereiro, D. Baldomir, M. Iglesias et al., Int. J. Quantum Chem. 81, 422 (2001).
58See supplementary material at http://dx.doi.org/10.1063/1.4754158 for cobalt ammonia association clusters $\text{Co}_{n}(\text{NH})_{m}$ generated by laser ablation of a cobalt foil target in the presence of 0.3% NH₃ mixed in the He expansion gas.