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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

THE JOURNAL OF CHEMICAL PHYSICS **137**, 124304 (2012)

Experimental and theoretical studies of ammonia generation: Reactions of H_2 with neutral cobalt nitride clusters

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

Ammonia generation through reaction of H_2 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. Co_mN_n clusters are generated through laser ablation of Co foil into N_2/He expansion gas. Mass peaks Co_mNH_2 ($m = 6$, 10) and Co_mNH_3 ($m = 7, 8, 9$) are observed for reactions of H_2 with the Co_mN_n clusters. Observation of these products indicates that clusters Co_mN ($m = 7, 8, 9$) have high reactivity with H_2 for ammonia generation. Density functional theory (DFT) calculations are performed to explore the potential energy surface for the reaction $Co_7N + 3/2H_2 \rightarrow Co_7NH_3$, and a barrierless, thermodynamically favorable pathway is obtained. An odd number of hydrogen atoms in Co_mNH_3 ($m = 7, 8, 9$) 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 NH_3 in a gas phase reaction. A catalytic cycle for ammonia generation from N_2 and H_2 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]

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]

Cobalt is an important transition metal, which has widely been used in ammonia synthesis as a catalyst modifier for various different alloy catalysts. The activity of iron catalysts for ammonia synthesis was found to increase markedly at lower temperatures with the addition of cobalt.[18–21] In studies of supported Ru–M (M = Fe, Co, Ni, Mo) bimetallic active center catalysts for ammonia synthesis, activity of the Ru–Co catalyst is the highest.[22] Recently, cobalt molybdenum nitride (Co_3Mo_3N), has attracted attention, as a result of its high efficacy in ammonia synthesis.[23–30]

Most catalysis studies are focused on condensed phase reactions, but a few related studies have also been carried out in gas phase. Reactions of neutral and charged cobalt clusters with hydrogen/deuterium have been investigated by several groups. Reactions of neutral cobalt clusters with D_2 in a fast flow reaction tube have been reported by Smalley and co-workers.[31,32] They measured the relative reaction rate constants for D_2 dissociation on various sized clusters and found a strong reactivity dependence on cluster size. Co_m clusters for $m = 4$-9 exhibit low reactivity with a minimum at $m = 6$, whereas $m = 3$, 10-28 clusters react much more efficiently. Persson and co-workers[33,34] also reported the reactions of neutral cobalt clusters Co_m ($m = 10$-45) with D_2 under near single collision conditions, using two reaction cells. The size dependence of the Co_m–D_2 reaction system was found to correspond well with the observations from experiments of the Smalley group. Ho *et al.*[35,36] have studied the gas phase reaction and saturated absorption on the surface of neutral cobalt clusters Co_m ($m = 7$-68), and found a similar D_2 reactivity dependence on cluster size for the cluster sizes reported by Smalley and co-workers. Absolute rate constants and reaction probabilities were also determined, and temperature

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dependence of the rate constants for dissociative adsorption of the first D_2 molecule to cobalt clusters Co_m (m = 9-21) was examined over the temperature range of 133-373 K.[35,36] The rate constants for clusters m = 10-13, 15-17 show no dependence on temperature, indicating that D_2 chemisorption reaction has no activation barrier. The rate constants for Co_9 and Co_{14} 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 Co_m^+ (m = 2-22) with H_2 was investigated using a fast flow reactor.[37] The reactivities of larger cationic cobalt clusters with H_2 are similar to the corresponding neutral cobalt clusters: reactivities of Co_m^+ (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 Co_m^+ (m = 2-16) with D_2 are studied by a guided ion-beam tandem mass spectrometer.[38] The observed products are Co_mD^+ for all clusters and $Co_mD_2^+$ for m = 4, 5, 9-16. The bond energies for Co_m^+–D are found to increase generally as the cluster size increases, and the bond energies of Co_m^+–D for larger clusters ($m \geq 10$) are found to be very close to the value for chemisorption of atomic hydrogen on bulk phase cobalt.

Reactions of cobalt clusters Co_m with H_2 are widely investigated in the literature, but the reactions of cobalt nitride clusters with H_2 have not been previously studied, although the dissociation of H_2 and formation of N-H bonds on catalysts are important steps for ammonia synthesis. In this report, the reactions of H_2 with cobalt nitride clusters Co_mN_n in a flow tube reactor are studied by 193 nm single photon ionization (SPI) coupled with time-of-flight mass spectrometry (TOFMS). Products containing an odd number of H atoms ($Co_{7\text{-}9}NH_3$) are found on the cluster series $Co_{7\text{-}9}N$, which suggests clusters Co_mN (m = 7, 8, 9) have high reactivity for H_2 for ammonia generation. Detailed reaction mechanisms for generation of NH_3 on $Co_{7\text{-}9}N_{1\text{-}3}$ 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.[39–42] Only a brief outline of the apparatus is given below. Co_mN_n clusters are generated by laser ablation of a cobalt foil target in the presence of 0.5% N_2 mixed in He expansion gas. A 10 Hz, focused, 532 nm Nd^{3+}:YAG laser (Nd^{3+}: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 H_2 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, H_2 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 $\sim 10^8$ s^{-1}.[43] Reactants and products are thermalized to 300-400 K by collision after the reaction.[44] 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/cm^2/pulse.

B. Calculational

Density functional theory (DFT) methods have been successfully employed to study structures and properties of the cobalt cluster system.[45] In this work, calculations of the structural parameters for neutral Co_mN clusters and the reactions of H_2 with these clusters are performed employing DFT as manipulated in the GAUSSIAN 09 program.[46] All the calculations are carried out with Becke's exchange[47] and Perdew–Wang's[48] correlation (BPW91) functional coupled with the modified LANL2DZ[49–52] 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.[53] To obtain a more precise description of Co_mN cluster structures, one would need to use a local spin density approximation and the generalized gradient approximation,[54,55] or a higher level of theory, such as CASSCF/MRCI calculations, which are successfully used to study structures and thermochemistry of iron sulfur clusters.[56]

The structures of Co_mN 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 Co_7N 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:[57,58] 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 Co_m (m = 1-18) clusters, and Figure 1(b) presents the

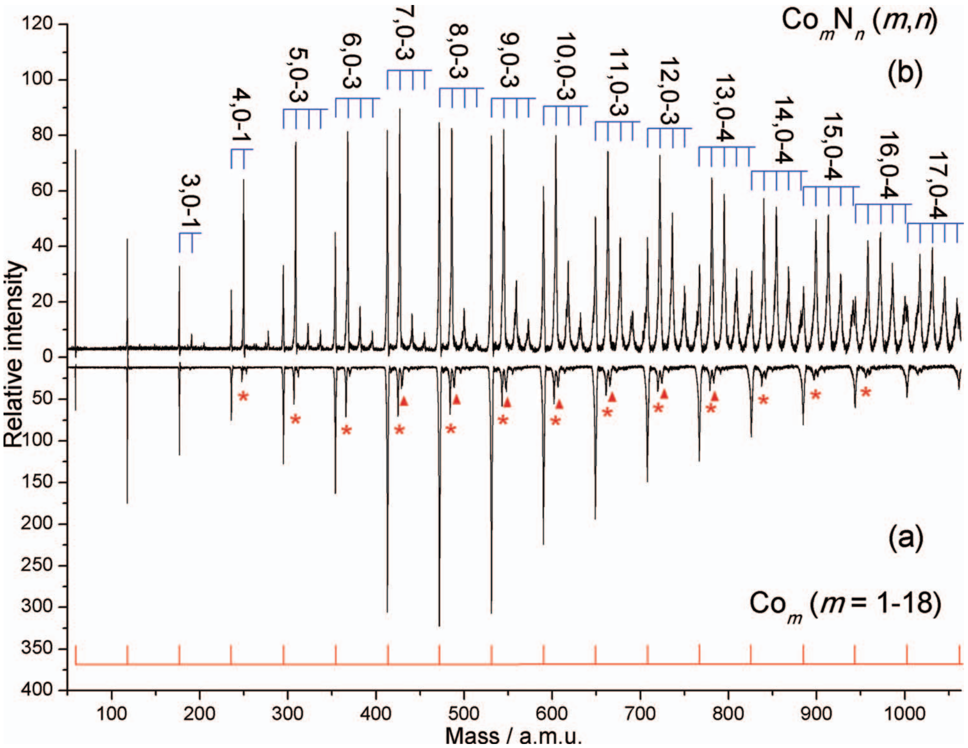

FIG. 1. Mass spectra of neutral (a) Co_m (m = 1-18); and (b) Co_mN_n (m = 1-17, n = 0-4) clusters ionized by a 193 nm laser. Clusters are generated by laser ablation of pure Co foil into (a) pure He, and (b) 0.5% N_2/He expansion gases at 75 psi backing pressure. The peaks marked with a star and triangle symbol are due to carbon and oxygen impurities, respectively.

TOF mass spectrum of neutral Co_mN_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 helium, and (b) pure helium seeded with 0.5% N_2 at 75 psi backing pressure. Some carbon and oxygen containing clusters (Co_mC and Co_mO) are also observed, due to trace amount of carbon and oxygen impurities in the metal or instrument system: if high purity helium carrier gas (99.995%) is employed for the expansion, the impurities are still present. Co_mN_n clusters are observed for $m \geq 3$: the maximum nitrogen atom number n in Co_mN_n increases from 1 to 4 as the cobalt atom number m increases to 17. The most intense mass peaks for each cobalt nitride series are Co_mN for $m = 3$-14, and Co_mN_2 for m = 15-17. Higher N_2 concentration backing gas was also prepared and used in the experiments: more nitrogen rich Co_mN_n clusters are observed at higher N_2 concentration.

Mass spectrum generated from the reaction of neutral cobalt nitride clusters Co_mN_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 Co_mN_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_mN signal decreases nearly to zero, and the products Co_mNH_2 (m = 6 and 10) and Co_mNH_3 (m = 7-9) are observed. Products $Co_{6,10}NH_2$ are generated from the association reactions,

$$Co_mN + H_2 \rightarrow Co_mNH_2, \qquad (1)$$

and are stabilized (cooled) by third body (usually He) collisions. For the products $Co_{7\text{-}9}NH_3$, 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_mN (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 $Co_7N + 3/2H_2$ 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),[59] 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; ρ is the reactant molecular density; Δt is the reaction time (~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 $\times 10^{-10}$ and 2.3 $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The absolute error in the values of the rate constants is ~50% based on an estimation of ρ and Δt in the experiments. The relative rate constants k^{rel} [$= k(Co_m + H_2)/k(Co_{15} + H_2)$] that are independent of the ρ and Δt 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_mH_x (x = 1, 3) are observed for

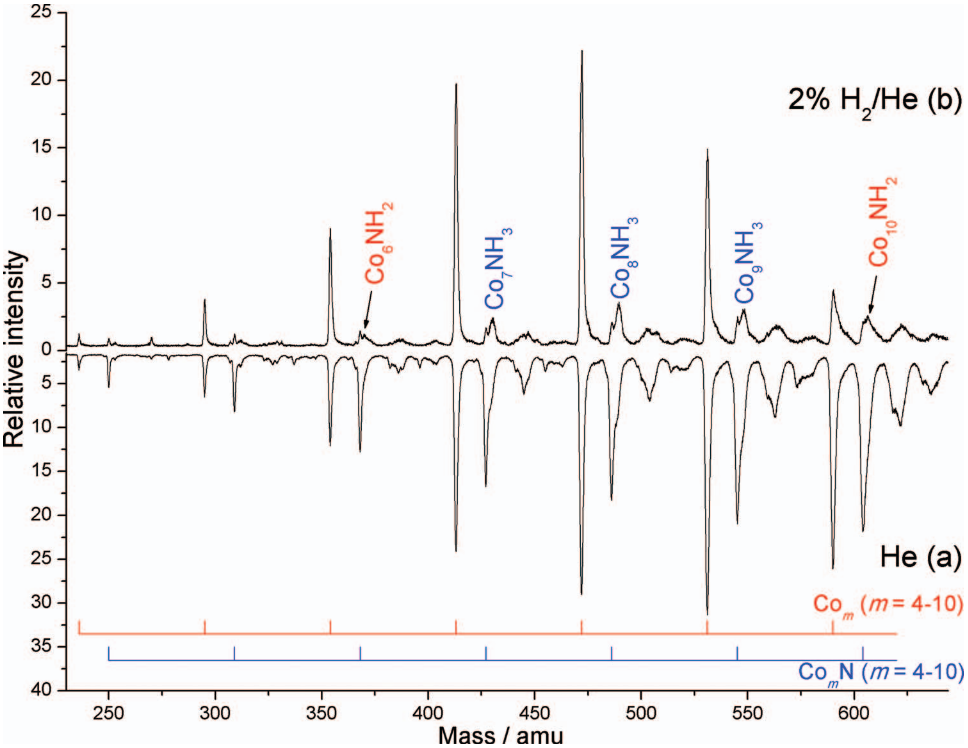

FIG. 2. Neutral cobalt nitride cluster Co_mN_n distributions after collision and reaction with (a) pure helium; and (b) 2% H_2/He in a fast flow reactor. Partial pressure of H_2 in the reactor is about 37 Pa for (b).

reaction of Co_m clusters with H_2, and only NH_3 adsorption products $Co_m(NH_3)_n$ are observed for reactions of Co_m with ammonia. Using the same approach, we can determine qualitative rate constants for the Co_mN clusters reacting with H_2 in the reaction cell. Assuming approximately second order kinetics, $k(Co_{6\text{-}10}N + H_2)$ values are estimated to be 8.4×10^{-9}, 8.4×10^{-9}, 7.8×10^{-9}, 7.7×10^{-9}, and 8.6×10^{-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 $Co_{1\text{-}7}N$ clusters. The nitrogen atom, in such structures for the $Co_{3\text{-}7}N$ 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 Co_2N (1.668 Å) distances. The bond lengths of three Co-N bonds in each cluster of $Co_{3\text{-}6}N$ are similar (<0.03 Å difference). For Co_7N, 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.

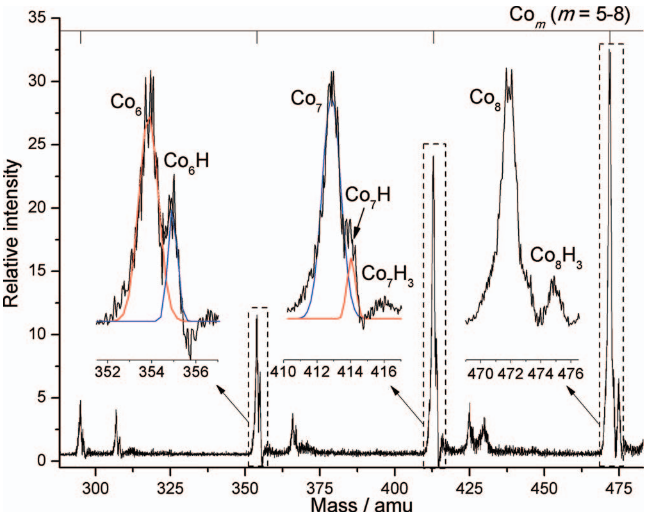

FIG. 3. Neutral cobalt hydride cluster $Co_{5\text{-}8}H_x$ distributions after collision and reaction with pure hydrogen gas in a fast flow reactor. The gaussian fitted peaks are given as the blue and red lines in the expanded layers.

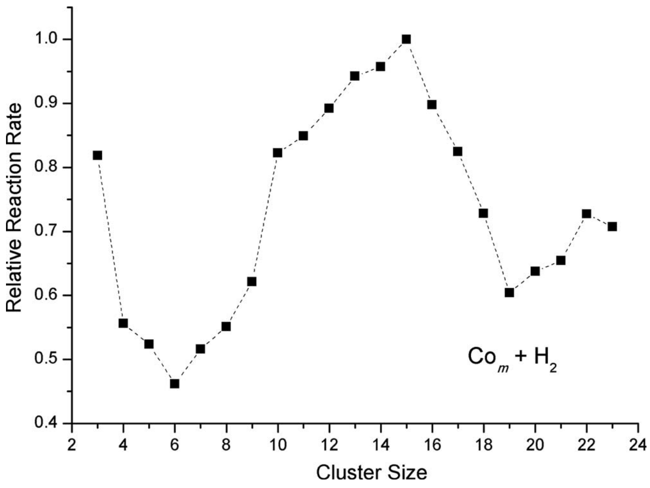

FIG. 4. Relative rate constants (k^{rel}) for reactions of H_2 with Co_m. The k^{rel} values are with respect to absolute rate constants $k(Co_{15} + H_2)$ (=2.3 $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

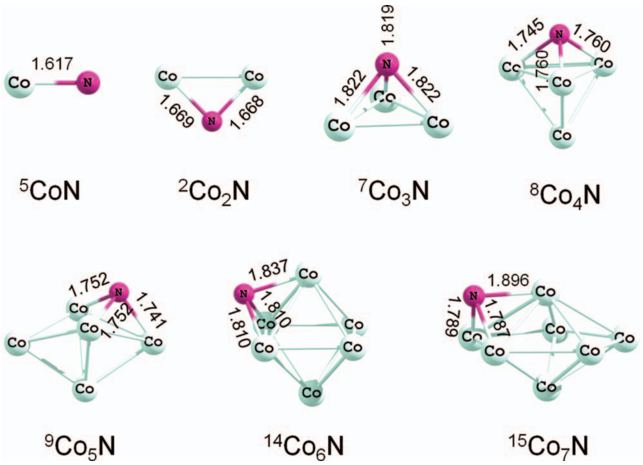

FIG. 5. DFT optimized structures of $Co_{1-7}N$ clusters. For each cluster, only the lowest energy structure with spin multiplicity (M) is listed as $^{M}Co_{m}N$; the Co-N bond length values in Å are given.

In order to study the mechanism for the ammonia formation reaction (H_2 with reactive $Co_{7-9}N$ species), DFT calculations are performed for the reaction $Co_7N + 3/2H_2 \rightarrow Co_7 + NH_3$ ($\Delta H = -0.73$ 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,

$$Co_7N + H_2 \rightarrow Co_7NH + H \quad (\Delta E = 1.27\,\text{eV}), \tag{2}$$

$$2Co_7N + H_2 \rightarrow 2Co_7NH \quad (\Delta E = -1.71\,\text{eV}). \tag{3}$$

As shown in Figure 6, the first step, formation of Co_7NH, is taken with a multiple molecular collision Reaction (3). The dissociative adsorption of H_2 on a Co_7NH cluster to form Co_7NH_3 (**I2**), is then an exothermic reaction. Every dissociated hydrogen atom of intermediate **I2** is adsorbed by two cobalt atoms, one of which connects with nitrogen. Via transition state **TS1**, one dissociated hydrogen atom transfers to nitrogen from the top cobalt site. The bond length of Co_{top}-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 (**I3**). The second hydrogen atom transfers to nitrogen via transition state **TS2** to form intermediate **I4**, in which the Co_{top}-N bond breaks, and the other two Co-N bonds length are increased from 1.855 Å to 1.949 Å. Through transition states **TS3** and **TS4**, the last hydrogen atom transfers to nitrogen and yields intermediate **I6**, for which the formed NH_3 moiety bonds to a Co atom with a 2.067 Å Co-N bond length. A stable intermediate $Co_7(NH_3)$ (1.68 eV lower than the initial energy) is formed, and finally generates product $Co_7 + NH_3$. Based on DFT calculations, the overall reaction of $Co_7N + 3/2H_2 \rightarrow Co_7 + NH_3$ is barrierless and thermodynamically favorable.

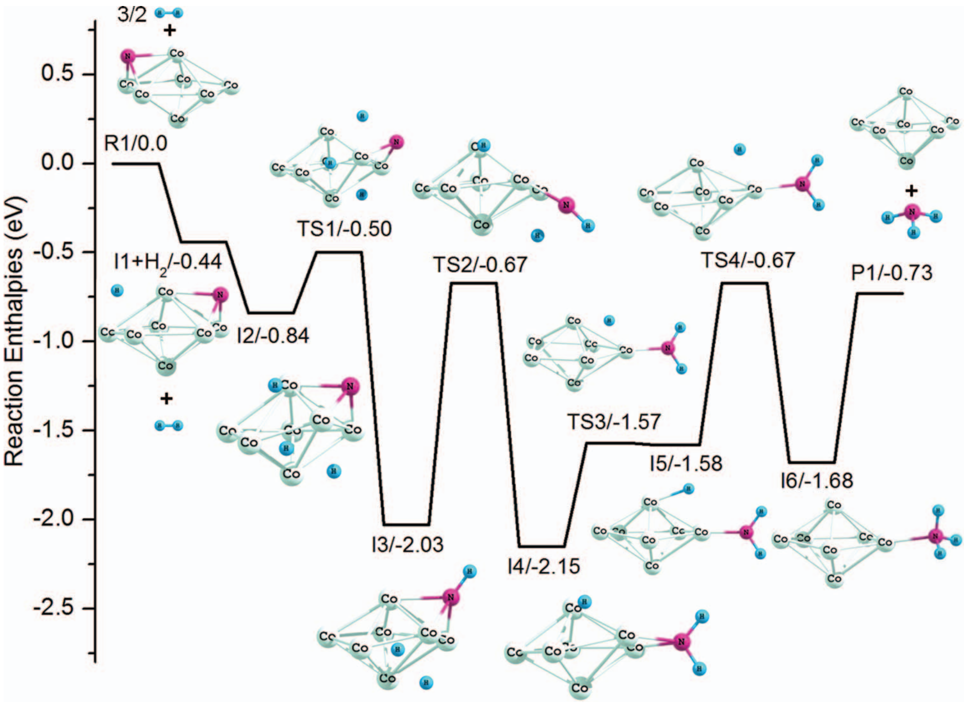

FIG. 6. A potential energy surface profile for the reaction $Co_7N + 3/2H_2 \rightarrow Co_7 + NH_3$. Energies are in eV and relative to the initial reactant energy of $Co_7N + 3/2H_2$. Energy levels are calculated by BPW91/modified LANL2DZ/6-311+G(d). See text for details.

IV. DISCUSSION

A. Reaction of Co_m clusters with NH_3 and H_2

Hydrogen chemisorption is one of the best known of all surface chemistries.[61–64] At room temperature, chemisorption states of H_2 on transition metal surfaces are dissociative, with the two hydrogen atoms well separated at different binding sites on the surface.[62,65,66] In this work, the reactions of neutral Co_m clusters with H_2 in the gas phase are studied in a flow tube reactor. The relative rate constants k^{rel} shown in Figure 4 indicate that the reactivity of neutral Co_m clusters with H_2 exhibits a strong size dependence. This observation corresponds well with the size dependence of the Co_m–D_2 reaction system reported previously.[31–34]

Figure 3 shows the Co_5 to Co_8 region of the Co_m mass distribution following Co_m collision and reaction with pure hydrogen gas. The details of the respective $Co_{6\text{-}8}H_x$ 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_7H (5.95 eV) and Co_7H_3 (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_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 $Co_7 + H_2 \rightarrow Co_7H + H$ ($\Delta E = 1.83$ eV). Thus, an odd number of hydrogen atoms for $Co_{6,7}H$ and $Co_{7,8}H_3$ must arise from multiple molecular collision reactions, in which the hydrogen molecule activation reaction occurs for two separate cobalt containing clusters: for example, $Co_7 + Co_7 + H_2 \rightarrow Co_7 + Co_7H_2 \rightarrow 2Co_7H$ ($\Delta E = -0.59$ 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,[41] products $(CH_2O)FeOH$ and FeOH are both observed due to multiple molecule collision reactions (e.g., $2FeO + CH_3OH$); for series reaction products $V_mS_nC_2H_5$ and V_mS_nH observed through multiple molecule collision reactions in the reaction of V_mS_n clusters with C_2H_4 and H_2;[39] and for reactions forming the cluster systems $M_mC_nH_x$ (M = Al, Be, Mg).[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 $Co_m(NH_3)_n$ are generated by laser ablation of a cobalt foil target in the presence of 0.3% NH_3 mixed in the He expansion gas (see Figure S1 of the supplementary material).[59] Cobalt ammonia association clusters $Co_m(NH_3)_n$ (m = 1-8, n = 1-9) are observed: $Co_m(NH_3)_m$ for m = 1-3, and $Co_m(NH_3)_{m\text{-}1}$ for m = 4, 5 are the most intense mass peaks for each series. No dehydrogenated clusters, such as Co_mN_n, are detected under these conditions. This result indicates the cobalt ammonia association clusters $Co_m(NH_3)_n$ are very stable and that Co_m will not react with (decompose) NH_3 to generate Co_mN_n or Co_mH_x.

B. Reaction of Co_mN clusters with H_2

Two types of reactions are identified for the interaction of Co_mN_n clusters with H_2 in the flow tube reactor experiments presented in Figure 2(b). First, association products Co_mNH_2 are observed for m = 6 and 10. Second, for m = 7-9, the species Co_mNH_3 are observed. This size dependent behavior indicates that diverse size dependent reactivities exist for the reaction of Co_mN_n clusters with H_2. The odd number of hydrogen atoms contained in products $Co_{7\text{-}9}NH_3$ should come from multiple molecular collision reactions, as determined through DFT calculations. Although the calculated VIEs for the lowest energy structures of Co_7NH (5.92 eV) and Co_7NH_3 (5.53 eV) are lower than the 6.4 eV single photon energy of 193 nm radiation, only Co_7NH_3 is observed for reaction of Co_7N with H_2: Co_7NH is not observed. This behavior is different from the reaction of pure cobalt Co_m clusters with H_2. For example, products $Co_7H_{1,3}$ are observed for reaction of Co_7 with H_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 $Co_{7\text{-}9}NH$ must be very reactive toward H_2 to form the more stable products $Co_{7\text{-}9}NH_3$. For m = 7-9, detection of the NH_3 moiety containing products indicates that the barrier for NH_3 moiety formation of intermediate products Co_mNH_3 must be lower than the initial reactant energy of $Co_mN + 3/2H_2$. In the flow tube reactor, Co_mN_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_3 moiety formation on $Co_{7\text{-}9}N$ clusters, products $Co_{7\text{-}9}NH$ or $Co_{7\text{-}9}NH_2$ should be observed in the mass spectrum (Figure 2); however, only the products $Co_{7\text{-}9}NH_3$ are detected. Thus, Co_mNH_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_3 moiety containing products, only association products $Co_{6,10}NH_2$ are observed for clusters m = 6, 10. Formation of the NH_3 moiety on cobalt nitride clusters Co_mN must involve a hydrogen atom transfer from cobalt to the nitrogen atom. From the structures of Co_mN displayed in Figure 5, the bond lengths of three Co-N bonds in Co_6N are similar (0.027 Å difference). For Co_7N, the bond length of Co_{top}-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_6N. A long bond length for a Co-N connection implies a low barrier for hydrogen atom transfer to nitrogen and initiation of the NH_3 moiety formation process. A similar and shorter bond length for the Co-N bonds in Co_6N may result

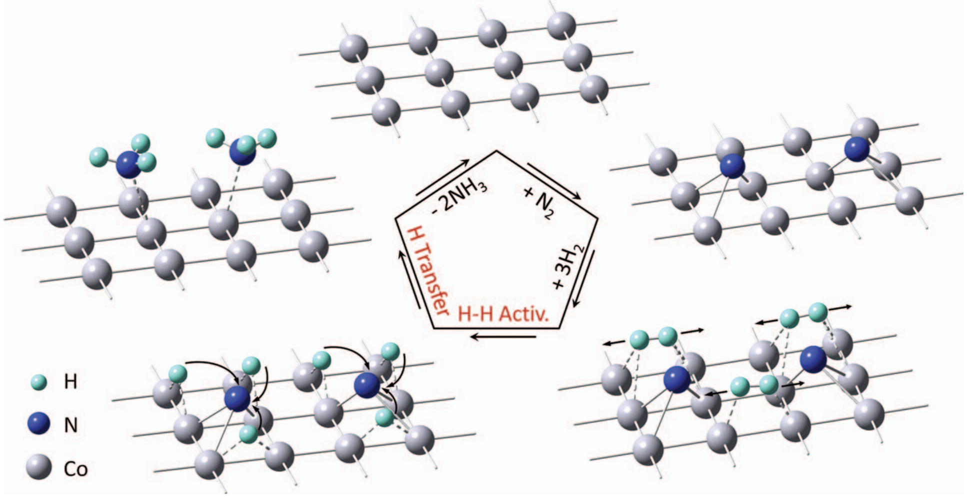

FIG. 7. Possible catalytic cycle for NH_3 formation from N_2 and H_2 over a cobalt metal catalyst surface at the molecular level.

in higher NH_3 formation barriers than the initial energy of $Co_{6,10}N + 3/2H_2$; thereby, only $H_2/Co_{6,10}N$ association products $Co_{6,10}NH_2$ are observed in the experiment.

C. Mechanism of ammonia formation on Co$_7$N cluster and proposed on cobalt metal catalyst surface

The observation of a stable Co_7NH_3 product in the reaction of Co_7N with H_2 suggests that NH_3 can be generated by the reaction $Co_7N + 3/2H_2 \rightarrow Co_7 + NH_3$. As the calculation results for the reaction pathways of NH_3 formation on the Co_7N 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 Co_mN 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 Co_mN clusters are the active sites for adsorption and dissociation of the hydrogen molecule in the NH_3 generation reaction. Then the next step in the ammonia formation reaction is the dissociated hydrogen atoms transfer to the N atom to yield the $–NH_3$ moiety in a stepwise process, and finally generate product $Co_7 + NH_3$. Free NH_3 molecules cannot be detected by single photon ionization from a 193 nm laser: the ionization energy of NH_3 is ~10.02 eV.[69] A hot NH_3 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, $Co_{7\text{-}9}N$ moieties are proposed to be active sites, which have high reactivity with H_2 for ammonia generation, based on our related gas phase studies. The key step for ammonia formation from reaction of neutral Co_7N clusters with H_2 is that an odd number adsorbed hydrogen atoms are generated from multiple molecular collision reactions. Thereby, this model system suggests that ammonia generation from N_2 and H_2 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 NH_3. 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 N_2 is a very difficult step due to the high bond energy for $N{\equiv}N$. Efficient N_2 activation requires more investigation, and should be considered in practical catalysis. H_2 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 $Co_{7\text{-}9}N$, have high reactivity with H_2 for ammonia generation.

V. CONCLUSIONS

Ammonia generation through reaction of H_2 with neutral cobalt nitride clusters in a fast flow reactor is investigated employing TOFMS and 193 nm SPI. Mass peaks Co_mNH_3 (m = 7, 8, 9) are observed for reactions of hydrogen with Co_mN_n clusters. Theoretical DFT calculations are performed to explore the potential energy surface for the reaction $Co_7N + 3/2H_2 \rightarrow Co_7NH_3$, and a barrierless, thermodynamically favorable pathway is obtained. The odd number of hydrogen atoms in Co_mNH_3 (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, $2Co_7N + H_2 \rightarrow 2Co_7NH$. 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 NH_3 in the gas phase reaction. Clusters Co_mN (m = 7, 8, 9) have high reactivity with H_2 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. FA9550-10-1-0454, and the National Science Foundation (NSF) through XSEDE resources under Grant No. TG-CHE110083.

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