

COMMUNICATIONS

Stepwise addition reactions in ammonia synthesis: A first principles studyChangjun Zhang, Zhi-Pan Liu, and P. Hu^{a)}*School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, United Kingdom*

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Catalytic ammonia synthesis is believed to proceed via dissociation of N_2 and H_2 with subsequent stepwise addition reactions from an adsorbed nitrogen atom to NH_3 . The first step, N_2 dissociation, has been thoroughly studied. However, little is known about the microscopic details of the stepwise addition reactions. To shed light on these stepwise addition reactions, density functional theory calculations with the generalized gradient approximation are employed to investigate NH_x ($x = 1, 3$) formation on Ru(0001). Transition states and reaction barriers are determined in each elementary step. It is found that the reaction barriers for stepwise addition reactions are rather high, for example, the barrier for NH hydrogenation is calculated to be 1.28 eV, which is comparable with that of N_2 dissociation. In addition, one of the stepwise addition reactions on a stepped surface is also considered. The reaction barrier is found to be much higher than that of N_2 dissociation on the same stepped surface, which indicates the importance of stepwise addition reactions in ammonia synthesis. © 2001 American Institute of Physics. [DOI: 10.1063/1.1384008]

The catalytic synthesis of ammonia has been one of the most extensively studied reactions in heterogeneous catalysis due to its great industrial and economic importance.^{1–3} It has long been realized that ammonia formation over catalysts proceeds via the dissociative adsorption of nitrogen and hydrogen, followed by stepwise additions, namely the hydrogenation of adsorbed nitrogen atoms and the intermediates, NH and NH_2 , over the surface in succession. Unfortunately, due to the complex nature of the reaction intermediates adsorbed on the surface, many aspects concerning the reaction processes in atomic level remain unclear. Although N_2 dissociation, which is generally believed to be the rate-determining step (RDS),^{4–6} has been extensively studied, little is known about the stepwise addition reactions microscopically.

Aiming at the development of a complete picture of ammonia synthesis, in this study we have performed density functional theory (DFT) calculations to investigate stepwise addition reactions, $N+H \rightarrow NH$, $NH+H \rightarrow NH_2$ and $NH_2+H \rightarrow NH_3$, on Ru(0001), a catalyst that has recently emerged as a commercially promising alternative to the traditional iron-based catalyst for ammonia synthesis.⁷ The DFT calculations were carried out with the generalized gradient approximation to describe the exchange and correlation effects.⁸ Ionic cores were described by ultrasoft pseudopotentials⁹ and the Kohn–Sham one-electron states were expanded in a plane wave basis set up to 340 eV. The supercell approach was employed to model periodic geometries. In order to minimize bonding competition^{10,11} between coadsorbed species on the surface, a large unit cell,

$p(3 \times 2)$, was used. The Ru(0001) surface was modeled by a periodic array of three layer slabs separated by ~ 11 Å of vacuum region. Monkhorst–Pack meshes with $2 \times 2 \times 1$ k -grid sampling in the surface Brillouin zones were used throughout. The adsorbed species were allowed to fully relax, while the substrate atoms were kept fixed at bulk truncated positions. Previous studies^{10–13} have revealed that the above setup provides sufficient accuracy. In addition, convergence with respect to the k -point sampling, the cutoff energy, and the number of slab layers has been checked using a $3 \times 4 \times 1$ k -point mesh, 400 eV, and four layers of Ru(0001), respectively. It was found that the calculated activation energy differs by less than 0.1 eV. Calculations were also performed in which the top layer of Ru atoms in the three-layer slab was allowed to relax. The structural difference of adsorbates between the relaxed and unrelaxed systems were found to be very small, typically ~ 0.01 Å. The activation energy difference between the relaxed and unrelaxed systems was calculated to be 0.06 eV, indicating the surface relaxation only has little effect on the calculation results. Transition states were searched using a constrained optimization scheme,¹⁰ and verified when (i) all forces on the atoms vanish and (ii) the total energy is a maximum with respect to the reaction coordinate and a minimum with respect to the remaining degrees of freedom.

Figure 1 shows the most stable initial state, transition state, and final state in each of the stepwise addition reactions. For comparison, certain structural parameters and chemisorption energies for the systems illustrated in Fig. 1 are summarized in Table I, together with the relevant data from the literature.^{14–18} It can be seen from Table I that agreement between our calculations and previously reported results is good. Figure 2 shows the energetic diagram for all

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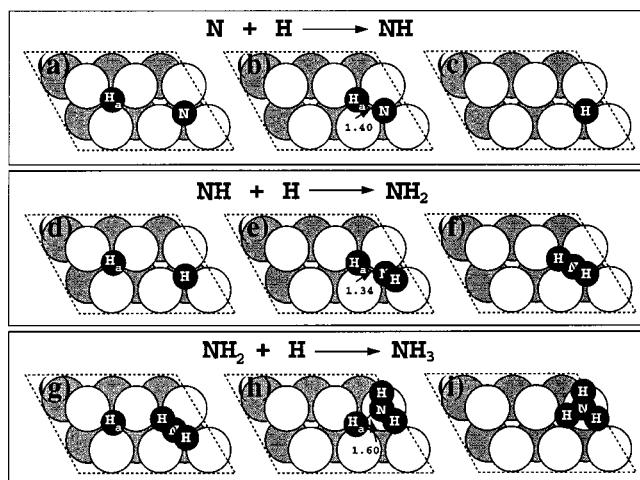


FIG. 1. Snapshots of the initial states, transition states, and final states in the $\text{NH}_x\text{-H}$ bond formation reactions. The dotted lines represent the unit cell. The data in the figure is the N-H_a distance (\AA), where H_a is the adsorbed H atom.

the forward and reverse elementary steps examined. The first hydrogenation step is found to be exothermic, the subsequent HN-H bond formation proceeds endothermically, and finally the NH_3 formation is again exothermic, which is consistent with the results obtained by Nørskov and co-workers.¹⁹ From Fig. 2, a striking feature can be seen: The reaction barriers for these three steps are surprisingly high. For example, the barrier of 1.28 eV for the HN+H reaction is comparable with a calculated value of 1.36 eV for N_2 dissociation,²⁰ the RDS step.

It is of interest to mention the experimental work of Dahl *et al.*²¹ They measured the overall reaction barrier for ammonia synthesis on Ru(0001) to be 101 ± 4 kJ/mol (1.05 ± 0.04 eV). The authors assumed that the first step, i.e., N_2 dissociation, was responsible for the measured barrier. However, they recently showed that with a fraction of a percent of steps on Ru(0001), N_2 dissociation takes place with an effective barrier of 0.4 eV, which is significantly lower than that of 1.36 eV obtained on terrace sites.²² The reason for this is that in the TS of N_2 dissociation at terrace sites, the two N atoms have to share one Ru atom (one N being close to the

TABLE I. Structural parameters and chemisorption energies of NH_x and H species in various systems from our calculations together with the relevant data (in parenthesis) from the literature.

	Adsorption height (\AA)	Intermolecular N-H bond length (\AA)	NH_x adsorption energy (eV)	H adsorption energy (eV)
N/Ru	1.09 (1.05 ± 0.05) ^a		5.70 ($5.82, 5.59$) ^a	
H/Ru	1.05 (1.10 ± 0.06) ^b			2.98 (2.90) ^c
NH/Ru	1.24 ($1.12\text{--}1.27$) ^c	1.014 ($1.028\text{--}1.039$) ^c	4.85 ($4.05\text{--}5.12$) ^c	
NH_2 /Ru	1.64	1.015	2.95	
NH_3 /Ru	2.179 (2.156) ^d	1.015 (1.029) ^d	0.89 ($1.14, 0.10$) ^d	

^aReference 14.

^bReference 15.

^cReference 16.

^dReference 17.

^dReference 18.

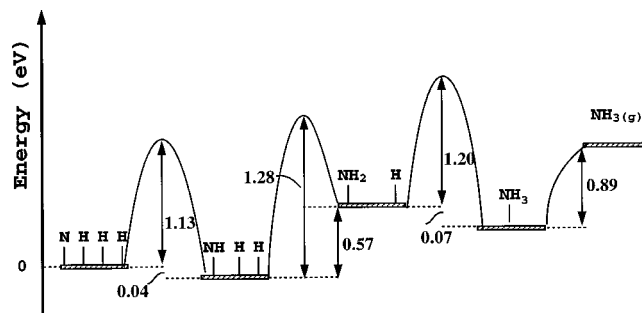


FIG. 2. Relative energy diagram for the surface reactions in ammonia synthesis on Ru(0001). The energy of coadsorption system of $\text{N}+3\text{H}$ is chosen as the reference energy (the zero point on the energy axis).

hcp site and another at a bridge site),²² which results in a large indirect repulsive interaction (bonding competition^{10,11}). On the other hand, on step sites, the two N atoms do not share bonding with any Ru atoms at nearest neighbors. Thus, the energy of TS at step sites is significantly lowered due to the considerable reduction of the bonding competition from terrace sites to step sites.²² Considering that there will always be a small concentration of steps on any real metal surface, it is therefore constructive to study the stepwise addition reactions at step sites. However, we expect that the reaction barrier change from terraces to steps for stepwise addition reactions would be smaller than that for N_2 dissociation. This is because of much smaller bonding competition in H addition reactions than N_2 dissociation on the terrace sites, considering much weaker bonding of H-Ru than N-Ru (Table I): The bonding competition between two adsorbates is related to their chemisorption energies; the stronger the chemisorption energies are, the higher the bonding competition is.

To verify the above speculation, we investigated the stepwise addition reactions on step sites by taking the $\text{NH+H} \rightarrow \text{NH}_2$ as an example, which has the largest reaction barrier on terrace sites. We first optimized all the possible initial states for NH and H co-adsorption on the stepped surface. We found that they have very similar energies. For example, the structure with NH being on the step edge and H being on the base of the step site differs from the structure with H being on the step edge and NH being on the base of the step site by only 0.08 eV in energy. We then located the transition state, which is schematically shown in Fig. 3. It can be seen that in the TS the NH species bonds with the bridge site of the step-edge and the H bonds with the Ru atoms on the terrace. There is essentially no bonding competition in this structure, as the NH and the H do not share metal atoms. The reaction barrier was calculated to be 0.81 eV, which is 0.47 eV lower than that on terrace sites. Considering a much larger difference of barriers for N_2 dissociation on step and terrace sites,²² therefore, the step sites do not play a significant role as in the case of N_2 dissociation on lowering the energies of TSs in the stepwise addition reactions. In other words, on a real catalyst on which steps always exist, the stepwise addition reactions would be important in determining the overall reaction barrier.

In addition to the high barriers for stepwise addition reactions found not only on terrace sites but also on step sites,

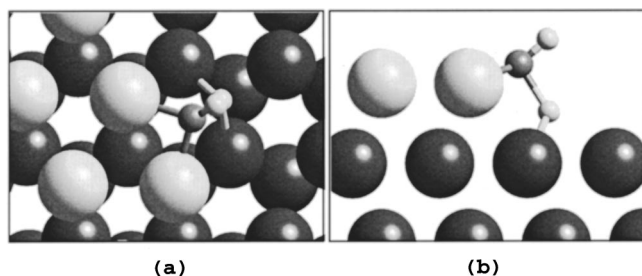


FIG. 3. Top (a) and side (b) views of the TS structure identified on the step site for $\text{NH}+\text{H}$ reaction. The Ru atoms in the first layer are the large white spheres, the rest of Ru atoms are the large dark spheres, the N atom is the small dark sphere and the H atoms are the small white spheres. For clarity, the top view is slightly tilted so that the H atom bonded with the base of the step site can be seen.

we also note that one of the reaction intermediates, NH_2 , is rather unstable. As shown in Fig. 2, of all the forward and reverse reactions, NH_2 formation has the highest barrier and NH_2 dehydrogenation the lowest. NH_2 is therefore difficult to form but relatively easy to dehydrogenate. This indicates that the concentration of adsorbed NH_2 during ammonia synthesis may remain very low. This result is consistent with the experiments of Shi, Jacobi, and Ertl²³ who found that the reaction intermediate NH_2 is not stable at 300 K. Hence, one can expect that the reaction, $\text{NH}_2+\text{H}\rightarrow\text{NH}_3$, in ammonia synthesis may be particularly important, because the NH_2 may be dehydrogenated if the reaction, $\text{NH}_2+\text{H}\rightarrow\text{NH}_3$, does not occur fast enough. It should be mentioned that to fully illustrate the reaction kinetics, the reaction barriers alone are not enough and reaction dynamics must be taken into account. In addition, the contribution from coverage effects is also important. However, this is beyond our present investigation.

In summary, this work represents the first attempt to study the microscopic pathways of the stepwise addition reactions and energetics in order to obtain a complete picture for ammonia synthesis. Our calculated geometries as well as energetics are in good agreement with experimental results,

where available. Based on our results, we suggest that the stepwise addition reactions are important in ammonia synthesis, which means that in order to improve ammonia synthesis the stepwise addition reactions cannot be neglected.

ACKNOWLEDGMENTS

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