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Abstract of Thesis

Name （HIDAYAT NOVIANTO NUR）	
Title	Effect of vicinal Ni(111) surfaces on N_2H_4-OH coadsorption system (ビシナル Ni(111)表面がN_2H_4–OH共吸着系に及ぼす影響)

Hydrazine (N_2H_4) has a high hydrogen content, making it a suitable fuel for energy applications. The initial bond cleaving in N_2H_4 plays a crucial role in the overall decomposition process. The N–N bond tends to be cleaved more easily than the N–H bond upon adsorption on most catalytic surfaces including Ni. This preferential N–N bond cleavage promotes the production of NH_2 reactive intermediates. This results in ammonia (NH_3) formation while at the same time reducing the hydrogen production efficiency. Hence, a mechanism to promote N–H bond cleaving over that of N–N is needed.

This study investigates the idea of using a stepped Ni surface and coadsorbed OH to facilitate N–H bond cleaving of N_2H_4. The stepped shape of the Ni surface introduces low-coordination sites, resulting in a unique spatial environment and electronic structure. These low-coordination sites not only enhance the adsorption strength of N_2H_4, but also allows it to form hydrogen bonding interactions with coadsorbed OH through unique configurations that are not feasible in flat surfaces. These hydrogen bonding interactions, assisted by the presence of the low-coordination sites, are expected to promote the N–H bond cleaving over that of N–N.

The first chapter of this thesis presents the study's framework, context and the general assumption as the scope of this thesis. Chapter 2 discusses briefly the basic theory and computational methods used in this thesis. Chapter 3 presents about N_2H_4-OH coadsorption configurations on the Ni(211) surface obtained from Density Functional Theory (DFT) calculations. The discussion begins from how vicinal steps and edges affect the stability of N_2H_4-OH coadsorption arrangements, comparing them to its respective individual molecular adsorption. Results suggest that the stabilizing relationship between N_2H_4 and OH coadsorbate to be mediated by hydrogen bonds. The most stable N_2H_4-OH configuration occurs perpendicular to the step direction, with N_2H_4 and OH occupying terrace and edge sites, respectively. The stability of N_2H_4 and OH coadsorbed on edge-sites is moderate, although it has the lowest N_2H_4 coadsorption and the longest hydrogen bond interaction distance. Placing N_2H_4 and OH respectively on edge and terrace sites slightly reduces their relative stability. However, this stabilizes the cis-conformation and causes considerable N-H bond elongations. These N_2H_4-OH coadsorption complexes are nearly equally accessible thermodynamically due to the relatively small energy differences (less than 0.2 eV). In an ideal extended periodic system at specific coverage used in this study, the obtained coadsorption configuration reveals the formation of a chain-like structure between N_2H_4-OH linked by hydrogen bonds with the potential of N–H bond cleaving.

Chapter 4 consists of the demonstration of the first N–H and N–N bond cleaving in N_2H_4 and OH coadsorption system on the Ni(211) surface via DFT-based calculations. Effects of the vicinal steps and edges in Ni(211) on the H-bond formation and the selectivity of each bond-cleaving reaction are demonstrated. The product of N–H bond cleaving is shown to be less stable than N–N bond cleaving. Nevertheless, the activation energy of N–H bond cleaving is demonstrated to be significantly lower than that of N–N. In an ideal extended periodic system at specific coverage used in this study, the results demonstrate the effect of utilizing a corrugated surface in promoting first N–H bond cleaving over that of N–N.

Chapter 5 discusses the idea of the generalized case of a corrugated surface, that is, a corrugated surface with larger terrace size. Larger terrace size makes the chain-like structure between N_2H_4-OH no longer possible. In this case, results suggest a difference in stability trend compared to the Ni(211) case in Chapter 3. Additionally, OH binds very strongly on the bridging Ni-Ni atoms of the edge site, which may possibly result in a more difficult N–H bond cleaving than the Ni(211) case. Hence, in this scenario, a corrugated surface with larger terrace size might have an adverse effect in promoting N–H bond cleaving.

様式 7

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

Hydrazine (N_2H_4) is a carbon-free energy carrier, and liquid hydrogen-storage material, making it a highly attractive material for energy applications. However, the intrinsically weaker N-N bond, as compared to the N-H bond, in N_2H_4 leads to the preferential production of NH_2 reactive intermediates, subsequent ammonia (NH_3) formation, and reduction in hydrogen (H_2) production efficiency. A mechanism that could selectively promote N-H cleavage over N-N cleavage would enable safer and more efficient hydrogen release, without forming explosive nitrogen gas mixtures. This could be compared to the use of N_2H_4 as a mild, tunable hydrogen/nitrogen donor in organic synthesis.

In this dissertation, the candidate explored the idea of using a stepped Ni surface and co-adsorbed OH to facilitate N-H bond cleaving of N_2H_4. The stepped shape of the Ni surface introduces low-coordination sites, resulting in a unique spatial environment and electronic structure. These low-coordination sites not only enhance N_2H_4 adsorption, but also fascilitate hydrogen bonding interactions with co-adsorbed OH, through unique configurations not feasible on flat surfaces. These hydrogen bonding interactions, assisted by the presence of the low-coordination sites, promote preferential N-H bond cleaving over that of N-N.

In Chapter 1, the candidate presented the framework, context, and the general assumptions of the study.

In Chapter 2, the candidate briefly discussed the basic theory and computational methods used in the study.

In Chapter 3, the candidate presented calculation results for OH, N_2H_4, and N_2H_4-OH adsorption on Ni(211). The candidate discussed how the vicinal steps and edges affect N_2H_4-OH co-adsorption, in comparison to individual molecular adsorption (i.e., [N_2H_4-OH]/ Ni(211), OH/Ni(211), and N_2H_4/Ni(211)). Results suggest that the hydrogen bonds mediate N_2H_4 and OH co-adsorption. This, in turn, results in the stabilization of the cis-conformation and considerable N-H bond elongation.

In Chapter 4, the candidate compared the cleaving of the first N-H and N-N bonds of the N_2H_4 and OH co-adsorbed on Ni(211). On Ni(211), the candidate confirmed the significantly lower activation energy for N-H bond cleaving, as compared to N-N bond cleaving. Based on the results, the candidate demonstrated the utility, explained the advantage and the utility of corrugated surfaces to preferentially facilitate N-H bond cleaving over the N-N bond.

In Chapter 5, the candidate presented and discussed the results for the case of a surface with a different surface feature, Ni(533). An increased terrace size alters the geometric and spatial constraints of the surface, resulting in a different stability trend compared to the Ni(211) case. OH binds strongly to the bridging Ni-Ni atoms at the edge site, resulting in more difficult N–H bond cleaving compared to the Ni(211) case. This results reiterated the importance of choosing proper surface features necessary to selectively promote N–H bond cleaving.

As described above, this dissertation contributes to a fundamental understanding of the effect of vicinal Ni(111) surfaces on N_2H_4-OH coadsorption system. This will make a significant contribution to applied physics, particulary in the understanding, development, and control of materials for energy applications. After careful considerations and discussions, the reviewers judged this paper to have value as a doctoral dissertation.