

— Article —

Molecular Orbital Study on the Oxidation Mechanism of Hydrazine and Hydroxylamine as Reducing Agents for Electroless Deposition Process

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The oxidation mechanism of hydrazine and hydroxylamine were investigated using molecular orbital (MO) calculation. Two pathways for their reactions were verified. One is initiated by hydrogen elimination from the reducing agent, followed by coordination of hydroxyl group to center nitrogen atom accompanied with electron emission. Another is initiated by coordination of hydroxyl group to hydrogen atom to form H₂O, which is eliminated later, followed by electron emission. The calculated results indicated that the oxidation reactions of hydrazine preferentially proceeded via the second pathway. It was also indicated that only the first electron emission steps of the hydrazine oxidation took place on Cu surface, while the following reactions proceeded at near the solid/liquid interface. The oxidation of hydroxylamine also proceeded via the elimination reaction of H₂O. After the oxidation, calculated heats of reactions suggested that OH radical, generated from N₂O as a product, decomposed hydroxylamine.

Key Words : Electroless Deposition Process, Molecular Orbital Calculation, Hydrazine, Hydroxylamine

1 Introduction

Electroless deposition process attracts much attention as an excellent tool for precise, micro and nano fabrication for various devices and systems.¹⁾ This process requires a reducing agent to supply electron for depositing metal species. The combination of reducing agent and metal species largely depends on the catalytic activity of the surface of deposited metal.²⁾ Hypophosphite ion, formaldehyde, and dimethylamine borane are known as representative reducing agents. Hydrazine also acts as a reducing agent, with which pure Ni film can be deposited.^{3,4)} Hydrazine has strongly negative redox potential as follows;



$$E_{\text{eq}} = -1.49\text{V vs. NHE}$$



$$E_{\text{eq}} = -1.16\text{V vs. NHE}$$

It thereby has capability to deposit Au, Co, etc.⁵⁻⁷⁾ Hydroxylamine, which also contains nitrogen, is expected to act as a reducing agent.⁸⁻¹⁰⁾

Although numbers of investigations for improvement of the bath stability and film property were reported,^{11,12)} analysis of the reaction mechanism is barely reported. Since there are various intermediates in this reaction, which is difficult to detect by experimental approaches, the reaction mechanism has not been resolved fundamentally. We have analyzed the reaction mechanism of various reducing agents using theoretical calculations.¹³⁻¹⁸⁾ In this work, the reaction mechanisms of hydrazine and hydroxylamine, both are nitrogen-based molecules, were

investigated at elementary step using *ab initio* molecular orbital (MO) calculation. First, we investigate the oxidation mechanism of hydrazine in an isolated state, and the oxidation mechanism on the Cu surface is also studied since catalytic activity of the metal surface plays a significant role for the electroless deposition process. Moreover, the oxidation mechanism of hydroxylamine is also investigated.

2 Computational method

An oxidation pathway of hydrazine,¹⁹⁾ proposed by van den Meerakker, starts from elimination of hydrogen atom, followed by electron emission after coordination of hydroxyl group as shown in Fig. 1. Alternative pathway, proposed by Harrison, proceeds from the elimination of H₂O followed by coordination of hydroxyl group for four times, as shown in Fig. 2.²⁰⁾

Based on these pathways, optimized geometry and energy of each intermediate were estimated using MO calculation, and the favorable reaction pathway was evaluated from the obtained energy diagram. The geometry of each intermediate was optimized at the Hartree-Fock

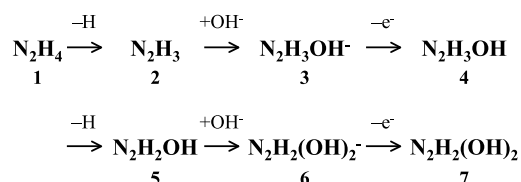


Fig. 1 The oxidation reaction scheme of hydrazine proposed by Meerakker.

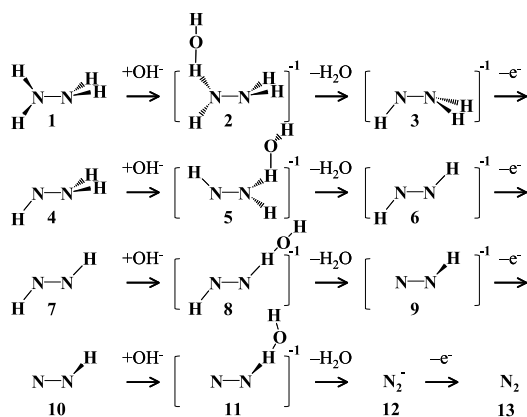


Fig. 2 The oxidation reaction scheme of hydrazine proposed by Harrison.

(HF) level. The optimization geometry of hydrazine corresponds to the geometry calculated at the same level by Habas.²¹ The electron correlation was taken into account for the single-point energy calculations by the Møller-Plesset 2nd perturbation (MP2) method.²² As for a model surface, Cu₄ cluster was employed. The cluster geometry is fixed in the Cu (111) crystal lattice position, with the bulk lattice constant of 2.556 Å. The calculations were performed using the Gaussian 98 rev a.9.²³ The Gaussian basis sets used in the present calculations were H/ cc-pVDZ, 6-31G **,²⁴ and N, O/ AUG-cc-pVDZ,²⁵ 6-31+G **,²⁶ For Cu, Ar core was replaced by an effective core potential by Hay and Wadt²⁷ and a valence electron was represented by a (5s5p4d)/[3s3p2d] basis set.

3 Results and Discussion

3.1 Reaction pathway of hydrazine in isolation system

First, the oxidation reaction pathway proposed by Meerakker was verified using the energy profile explained above, as is shown in Fig. 3. The values shown in open circles are obtained by reducing the stabilization energy from values shown in solid ones, which are equal to heat of formation for hydrogen gas during the oxidation reaction of hydrazine. Figure 3 shows the energy barriers in the pathway of N₂H₄ → N₂H₃OH⁻ (1 → 3) and N₂H₃OH⁻ → N₂H₂(OH)₂⁻ (4 → 6) decrease by the stability of hydrogen gas generation. However, both energy barriers remain high and heat of reaction in the whole reaction (1 → 7) is *ca.* 200 kJ/mol. From these results, it is difficult for the reaction to take place via this pathway. The result implied instability derived from the geometry of hydrazine where hydroxyl group directly coordinated to the center atom.

On the other hand, Harrison proposed the pathway in which hydroxyl group did not coordinate to nitrogen atom but hydrogen atom, to form H₂O, which is eliminated later.²⁰ Following this, the energy profile for the pathway was estimated as shown in Fig. 4.

According to the results shown in Fig. 4, the energy barriers were lower than those shown in Fig. 3, and the calculated value of the heat of reaction (1 → 13) was suffi-

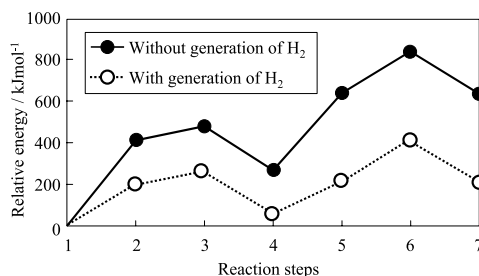


Fig. 3 Energy diagram for the oxidation reaction process of hydrazine proposed by Meerakker.

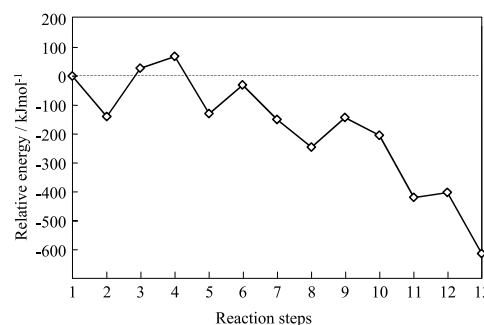


Fig. 4 Energy diagram for the oxidation reaction process of hydrazine proposed by Harrison.

ciently low, suggesting that the oxidation reaction of hydrazine takes place via elimination reaction of H₂O accompanied with direct coordination of hydroxyl group to hydrogen atom, rather than H-OH⁻ substitution reaction accompanied with direct coordination to nitrogen atom. Furthermore, it was suggested that solvation effect was an important factor so that the oxidation reactivity of hydrazine depended on the formation of H₂O with hydroxyl group.

3.2 The reaction mechanism of hydrazine on Cu surface

The oxidation mechanism of hydrazine on Cu surface was investigated, based on the reaction scheme described in Fig. 2. Figure 5 shows the energy profile for the oxidation of hydrazine at the Cu surface. Although initial oxidation reaction from N₂H₄ to N₂H₃ takes place through the adsorption to the Cu surface, following reaction to form N₂H₂ from N₂H₃ is unstabilized through the adsorption. Moreover, no stabilization effect of the Cu surface is observed during the reaction from N₂H₂ to N₂. These results indicate that the Cu surface catalyses only the initial step of the hydrazine oxidation, and following reactions do not take place on the Cu surface. In other words, Cu surface will receive only one electron from the first step of the hydrazine oxidation reaction, which triggers the following reaction explosively over the deposited Cu surface/liquid interface.

3.3 The oxidation mechanism of hydroxylamine

Following the concepts described above, the oxidation reaction of hydroxylamine, which is initiated by elimination of hydrogen atom followed by electron emission with coordination of hydroxyl group, is proposed as

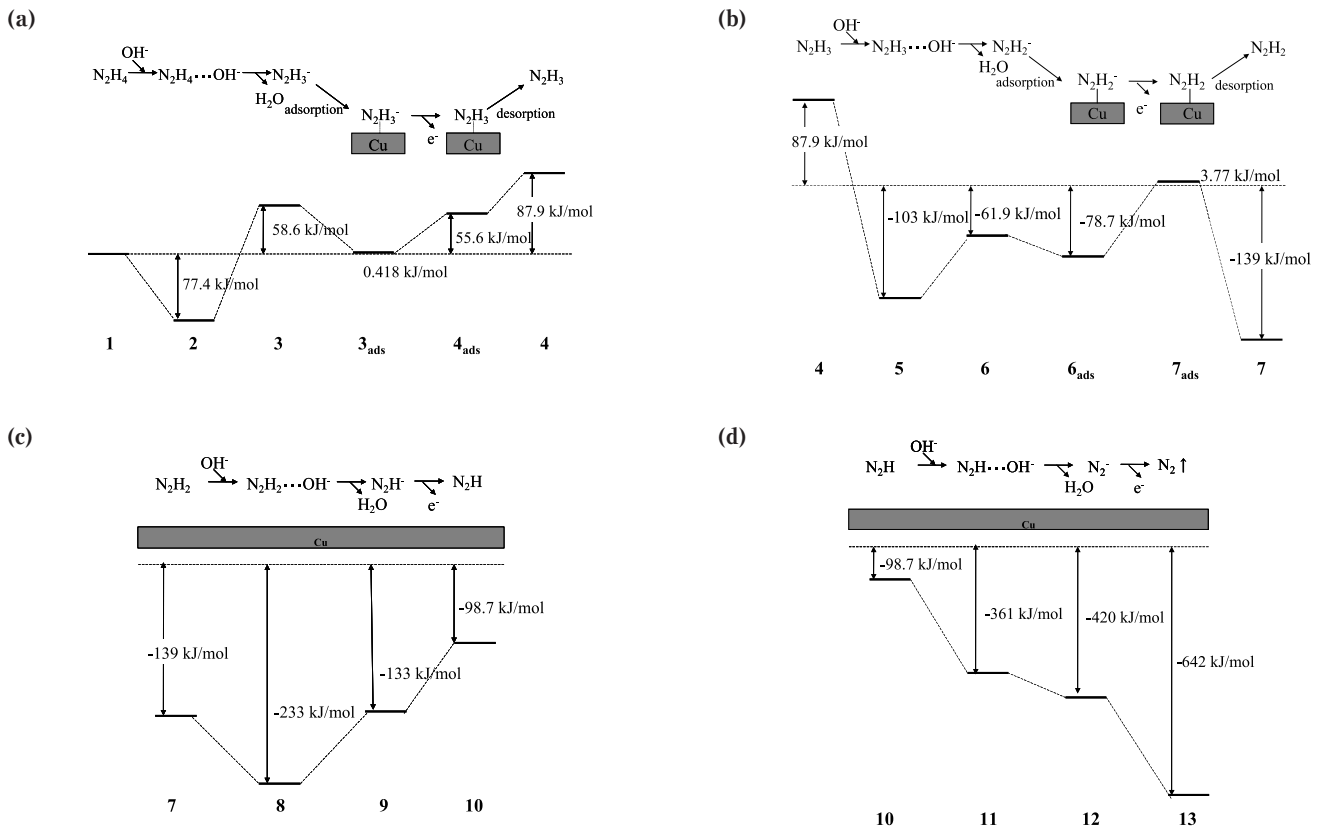


Fig. 5 Energy diagram for the oxidation reaction process of hydrazine on Cu surface proposed by Harrison. (a): $\text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3$, (b): $\text{N}_2\text{H}_3 \rightarrow \text{N}_2\text{H}_2$, (c): $\text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}$, and (d): $\text{N}_2\text{H} \rightarrow \text{N}_2$.

shown in Fig. 6. The energy profiles for this reaction are shown in Fig. 7.

Open and solid circles in Fig. 7 represent the same condition as Fig. 3. Figure 7 indicates that heat of formation in the overall reaction for both cases are so high that the overall reaction is not stabilized. Thus, the energy profile was re-created according to Harrison's proposal pathway that proceeded with coordination of hydroxyl group to hydrogen atom, elimination of H_2O , and electron emission.²⁰⁾

Figure 8 (a) indicates that H_2O elimination reaction does not occur spontaneously in the oxidation of hydroxylamine, whereas oxygen atom of hydroxyl group attacked to hydrogen atom of hydroxyl group of hydroxylamine ($\text{NH}_2\text{OH} \cdots \text{OH}$: -105 kJ/mol), and then the reaction proceeds via the reaction intermediate without hydroxyl group (NOH_2 : +12.5 kJ/mol). The energy barrier of transfer reaction between the intermediates with or without hydroxyl group ($\text{NH}_2\text{OH} \leftrightarrow \text{NOH}_3$) is so high that the reaction does not take place. Figure 8 (b) indicates that the hydrogen elimination reaction via $\text{O}=\text{NH}$ toward generation of N_2O proceeds more smoothly than that via $\text{N}-\text{OH}$.

Hydroxyl group did not attack to nitrogen atom of hydroxylamine but to hydrogen atom to form H_2O same as hydrazine. Since the oxidation number of nitrogen atom is saturated compared with other reducing agent such as boron and carbon atoms, nitrogen atom does not bond with hydroxyl group directly.

After the oxidation reaction mentioned above, N_2O as

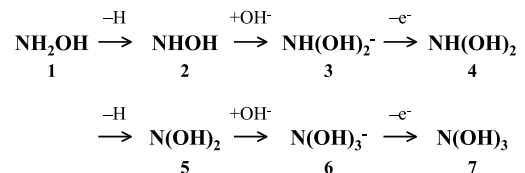


Fig. 6 The oxidation reaction scheme of hydroxylamine.

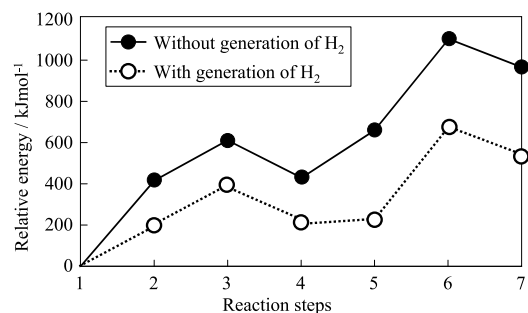
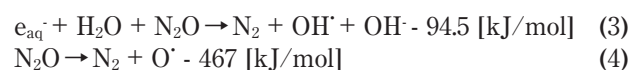


Fig. 7 Energy diagram for the oxidation reaction process of hydroxylamine.

a product was generated as shown in Fig. 8. It was reported that the N_2O reacts in the solution as follows,²⁸⁾



Here, heat of formation were calculated by MO calculation.

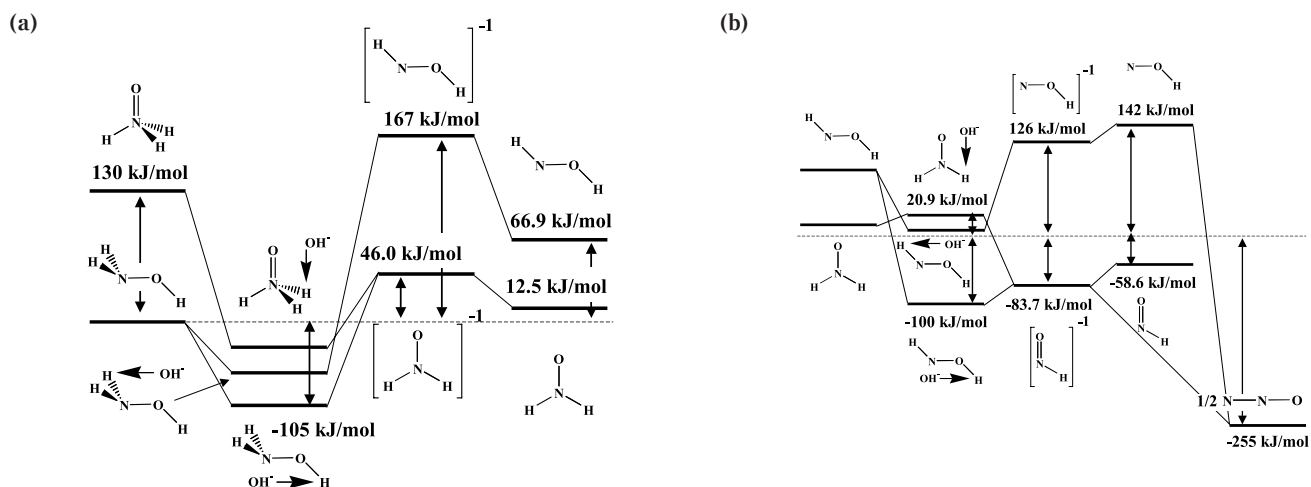
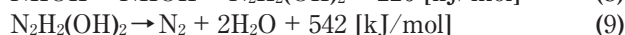


Fig. 8 Energy diagram for the oxidation reaction process of hydroxylamine. (a): $\text{NH}_2\text{OH} \rightarrow \text{NOH}_2$ and (b): $\text{NOH}_2 \rightarrow \text{N}_2\text{O}$.

N_2O dissociated to OH or O radical. Moreover, O radical attacked to H_2O to form H_2O_2 , and then H_2O_2 dissociated to OH radical as follows.²⁹⁾



Experimental results indicated that following reactions take place with the OH radical.³⁰⁾



These reactions were exothermic with large heat of reaction to trigger the explosive reaction. Indeed, pH steeply rises before the explosion. It was suggested that the OH radical was formed and attacked to hydroxylamine to decompose without electron emission.

In order to stabilize the bath containing hydroxylamine, additives are required to remove the OH radical. For instance, small amount of organic compounds added into the solution to react with OH radical preferentially. By consuming the radical, the reaction between OH radical and hydroxylamine was prevented.

4 Summary

We have investigated the reaction mechanisms of hydrazine and hydroxylamine, which are reducing agents containing nitrogen atom for electroless deposition processes, using MO method. We evaluated preferable reaction pathways of each agent. Calculated energy profiles indicated that the oxidation pathways of each agent in an isolated system did not proceed via the substitution reaction of $\text{H} \leftrightarrow \text{OH} \cdot$ but the coordination of OH to H to form H_2O , which is eliminated later. It was also indicated that Cu surface catalyzed only the first step of electron emission for the hydrazine oxidation. Moreover, it was suggested that N_2O , as a product of the hydroxylamine oxidation, generated OH radical, which triggered the explosive reaction with hydroxylamine itself.

As described, by using MO method, difference

between nitrogen-based reducing agents and other agents were clarified. To develop the electroless deposition process, it is needed for estimation of the property for various reducing agents by theoretical analysis.

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