

Density Functional Theory Study on the Oxidation Mechanisms of Aldehydes as Reductants for Electroless Deposition Process

K. Sakata¹, T. Shimada¹, H. Nakai²,
T. Homma¹, T. Osaka¹

¹ Department of Applied Chemistry,

² Department of Chemistry,

Waseda University

3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Electroless deposition process is a powerful technique to form various functional surfaces for electronic devices and systems. In order to elucidate its mechanism to achieve further precise control of the properties, numbers of studies have been carried out mainly by experimental approaches. However, the reaction mechanism is so complex that a reasonable model has not been established yet. Therefore, we have been studying the electroless deposition process by Molecular Orbital (MO) and Density functional theory (DFT) calculations, which can investigate oxidation reaction process of reductants (including their intermediate species) and catalytic activity of metal surface at an element level¹⁻³.

In this study, we focus upon aldehydes as the reducing agent, which are mainly used for electroless copper deposition. We investigate the oxidation mechanisms of aldehydes, *i.e.*, formaldehyde ($HCHO$), acetaldehyde (CH_3CHO), and glyoxylic acid ($COOHCHO$) to study the functional group effect for the reaction processes.

All DFT calculations were performed using the B3LYP method as implemented in the GAUSSIAN 98 package. As for a model surface, $Cu_{22}(111)$ cluster was used. Cu–Cu distance was fixed at its bulk lattice value of 2.556 Å. The Gaussian basis sets were 6-31G** for carbon and hydrogen, 6-31+G** for oxygen in which diffuse functions, and Hay & Wadt for Cu were used.

First, we investigated three kinds of the aldehydes to clarify their oxidation mechanisms in isolated state. Van den Meerakker proposed a general reaction pathway, in which the reaction proceeds via three-coordinate intermediate species, initiated by dehydrogenation⁴. On the other hand, we have proposed the reaction pathway via five-coordinate species, initiated by addition of OH^{-1} ³. By comparing the energy diagram of the reaction pathways via three-coordinate and five-coordinate by relative energy on the basis of reactants, it was indicated that the oxidation reactions of the three aldehydes on the Cu surface took place via five-coordinate pathway, rather than via-three coordinate one.

Next, in order to investigate the reaction mechanism more in detail, the effect of solvation was investigated, which was taken into account by the self-consistent reaction field method with an isodensity polarized continuum model (SCRF-IPCM). It was indicated that the reactions of the three aldehydes are endothermic in the bulk solution, whereas the reactions are exothermic in the vicinity of the metal/liquid interface, suggesting that the oxidation reaction of aldehydes proceeds preferentially at the metal surface region.

Furthermore, their oxidation mechanisms at the metal surface were also studied since the catalytic activity of the metal surface is one of the most important issues for the electroless deposition reaction. For this, adsorption energy and desorption energy of three aldehydes were estimated, and from the results, it was suggested that glyoxylic acid,

whose functional group is electron-withdrawing, tend to adsorb weakly onto the Cu surface.

Then, in order to explain the origin of the smaller adsorption and desorption energy of glyoxylic acid than other aldehydes, we investigated the local interaction between Cu surface and three aldehydes by Energy Density Analysis (EDA)⁵, which is able to estimate the energies of each atom of molecule.

The results of EDA analysis indicated that small interaction between glyoxylic acid and Cu surface results in the smaller adsorption and desorption energy of glyoxylic acid, suggesting the effect of substitution of the functional group on the oxidation mechanism.

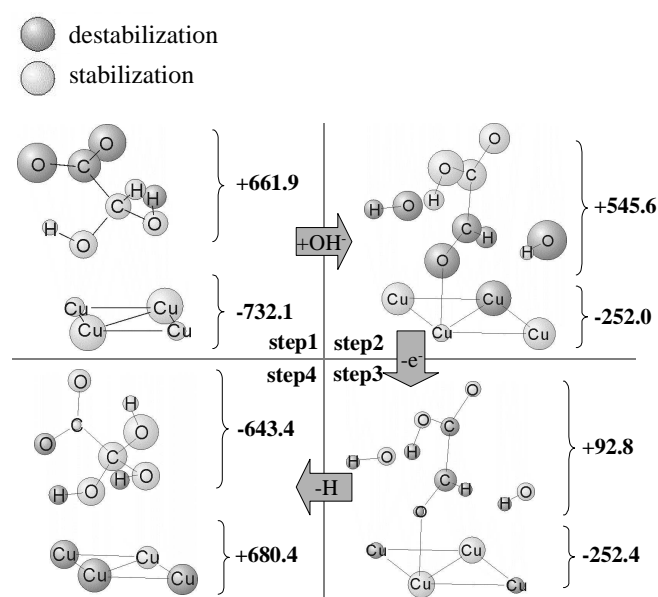


Figure 1 Energy difference [kJ/mol] among each step of oxidation. The energy is divided into glyoxylic acid and metal by using Energy Density Analysis. (via five-coordinate pathway)

References

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