Theoretical study of correlations between structures and catalytic activities in polymer-stabilized Au nano cluster catalysts

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Abstract: Polymer-stabilized Au nano clusters (Au NC), Au:PVP and Au:PAA catalyze aerobic oxidation of alcohols and the catalytic activity of Au:PVP is much higher than that of Au:PAA. To elucidate the correlations between catalytic activities and structures in them, we performed both DFT and MD calculations of Au_{38} model cluster and protective polymers formed by 144 molecules of monomers. We established an easy method to optimize temperature parameters in replica exchange molecular dynamics. The results showed that the number of open active sites on Au NC surface without the polymer adsorption was a good index to predict catalytic activities.

Keywords: Au catalyst, Replica exchange molecular dynamics, Data science

1. Introduction

Au NC exhibits unique properties when it is deposited on selected supports (TiO_2, Fe_2O_3etc.). In these catalysts, various catalytic reactions are discovered such as selective oxidation of organic compounds, oxidative Cross-Coupling etc. Polymer-stabilized Au NC catalysts maintain their stabilities and catalytic activities in liquid phase, as if it were in gas phase; this is because the polymer covering Au NC has an affinity for water. Fortunately, protective polymer loosely forms a coordinate covalent bond with Au NC surface, which hardly affects catalytic nature of Au NC. This model catalyst makes it possible to escape explicitly discussing electronic states of supports in detail, which is very convenient in casting new light on catalytic reaction mechanism for Au NCs. As an electron donor, the polymer also indirectly activates O_2 molecules in aerobic oxidation reactions, while inhibiting the binding of substrates to active sites on Au NC; the choice of protective polymer takes on considerable importance. Previously, Tsukuda et al. reported that Au NCs stabilized by poly(N-vinyl-2-pyrrolidone) [PVP; $(C_6H_9ON)_n$], abbreviated to Au:PVP , can oxidize p-hydroxybenzyl alcohol selectively into the corresponding aldehyde in water without degradation; they also reported that poly(allylamine) [PAA; $(C_3H_5NH_3)_n$], abbreviated to Au:PAA behaves like Au:PVP, but the catalytic activity of Au:PVP was much higher than that of Au:PAA[1]. To elucidate this difference, we investigated the difference in substrate accessibility on Au NC surface by using DFT and MD calculations.

2. Theoretical

To assess the arrangement of adsorbed active sites on Au NC which resulted from heterojunction between Au NC and H_2O or polymers, DFT calculations with Perdew–Burke-Ernzerhof functional were performed, with applying Plane wave basis set and PAW (Projector-Augmented Wave function) method for all atoms under the condition where the cubic supercell was a 30 Å on a side. For these supercell-gamma point calculations, VASP program suite was used; Au NC, PVP, and PAA were modeled in Au_{38} cluster, 144 molecules of ethylpyrrolidone(EP), and propanamine (PA) respectively. To find all active sites on Au_{38} cluster, the maximum number of adsorbed H_2O molecules and its arrangement on Au NC surface were investigated. It was found that there were 8 active sites on Au_{38} cluster, and the combinations of heterojunction by H_2O and EP or PA were also estimated from the viewpoint of adsorption energy. Under the Boltzmann distribution at 300K, model molecules of Au:PVP and Au:PAA were narrowed down to one respectively. While the best number of heterojunction between Au_{38} and EP was 4, the most reasonable number of heterojunction between Au_{38} and PA was 8, which was taken as a guide to split protective 144-

mer polymer into some oligomers. For MD calculations, as concrete model molecules of Au_{38}:PVP_{144} and Au_{38}:PAA_{144} in MD calculation, $Au_{38}:(PVP_{36})_4$ and $Au_{38}:(PAA_{18})_8$ were chosen. MD simulations for Au:PVP and Au:PAA were performed to compare the difference in substrate accessibility on the Au NC surface. Through this simulation, Au NC surface coverage ratios by protective polymers were directly calculated and assessed by using replica exchange MD (T-REMD) in AMBER 14 program and multivariate analysis.

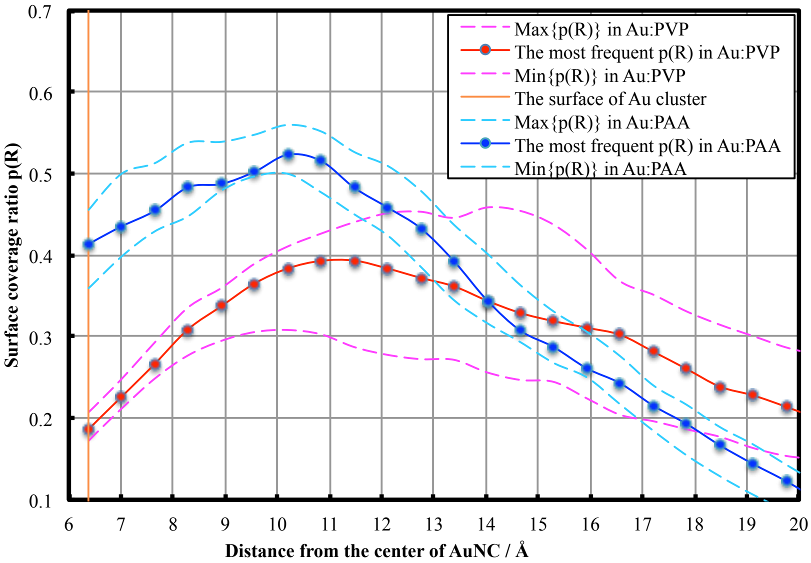

Figure 1. The most frequent radial occupancy distributions (ROD) and its fluctuation for $Au_{38}:(PVP_{36})_4$ and $Au_{38}:(PAA_{18})_8$

3. Results and discussion

In our previous study, we used smaller model molucules Au_{13}:PVP_{36} and $Au_{13}:(PAA_4)_9$, and reported that the difference in maximum value of the ROD was important index to estimate the catalytic activity, but this difference was hardly increased in larger model molecules in this study[2]. In our calculation, the difference was 13.0%, and we concluded that the index was not important because the radius point of maximum ROD was far from Au NC surface and the maximum value at that point had little effect on substrate accessibility on Au NC surface. On the other hand, in a first coordination area ($6.37<R<7.01$;Fig.1), the difference of the surface coverage ratio was 22.7%; this is more conspicuous difference, and considering that the catalysis exists in a solution of substrate, the surface coverage ratio in a first coordination area is more important information to predict the high/low relation of the catalytic activity. The high/low relation of surface coverage ratios in a first coordination area is mainly decided by the number of adsorbed heteroatom on Au NC, rather than by the bulkiness of protective polymer and the ease of main chain rotation. Thus, the difference of the surface coverage ratio in a first coordination area explains the many/few relation of open active sites on Au NC without the polymer adsorption.

4. Conclusions

The high/low relation of the catalytic activity of polymer-stabilized Au NCs can be predicted only by the number of adsorbed monomer molecule on Au NC in DFT calculation. The more monomer molecules adsorbed on Au NC, the less active sites there were. It was concluded that the difference of the number of adsorbed monomer molecule on Au NC was a good index to predict the high/low relation of the catalytic activity.

References

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