



Non-bonding and bonding interactions of biogenic impurities with the metal catalyst and the design of bimetallic alloys



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ABSTRACT

Interaction of biogenic impurities with the Ni (111) catalyst surface was studied to understand their important role in inhibiting catalysis. Non-bonding interactions of amino acids (Alanine (Ala), Cysteine (Cys), Methionine (Met), Tryptophan (Trp), Histidine (His), Lysine (Lys), Glutamic acid (Glu) and Threonine (Thr)) in aqueous environment were examined using classical molecular dynamics (MD) simulations. The potential of mean force (PMF) profiles of amino acids revealed qualitative differences, resulting into altered orientation and the choice of preferential interacting site with the metal surface. The side chains of all the amino acids were observed to align parallel to the metal surface. Amino acids containing sulfur (Met and Cys) and heterocyclic nitrogen (Trp, His) were observed to interact favorably with the Ni surface. Most of the preferential interacting sites were observed to be in direct contact with the surface except Lys which interacted with the backbone nitrogen oriented away from the surface. The strength of non-bonded interactions varied from -13 to -71 kJ/mol with Ala as the weakest and Trp as the strongest interacting amino acids. The interaction energies scaled linearly with the solvent accessible surface area of the amino acids. Density functional theory (DFT) calculations were utilized to understand the bonding interactions of sulfur (S) containing amino acids (Met and Cys) and the irreversible catalyst deactivation caused by them. DFT calculations showed strong binding for both Cys (-123 kJ/mol) and Met (-115 kJ/mol), undergoing dissociation to form atomic S on the Ni (111) surface with an intrinsic activation barrier of 32 kJ/mol and 133 kJ/mol, respectively, for the C–S bond cleavage. However, the mechanistic routes for dissociation followed by the two amino acids were a bit different. While in Cys, the C–H activation was followed by C–S cleavage, in Met, C–S bond was activated first to form S-CH₃ species on the catalyst surface. In contrast to Met at higher coverage, Cys was observed to decompose to elemental S on the surface. The mechanistic insights thus obtained lead to an explorative theoretical framework for the design of a bimetallic catalyst, which may be used in an integrated bio and chemo-catalytic process with reduced chances of deactivation. The Ni–Au alloy surface showed lower binding energies for both Met (-88 kJ/mol) and S (-132 kJ/mol), as compared to pure Ni surface, indicating promising prospects for the activity of such an alloy catalyst.

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1. Introduction

Emerging trend in heterogeneous catalysis research for biorenewable products is focused on the integration of the bio- and

chemo-catalytic processes to harness the potential biomass source for producing fuels and chemicals [1–4]. To achieve this goal, the reactions are generally carried out in liquid phase, wherein biogenic impurities (e.g. amino acids and protein residues) of the fermentation process pose a challenge, leading to catalyst deactivation and poor yield of the desired product [5]. Recent publications by Dumesic and co-workers have highlighted this problem and suggested remedies such as polymer coating of the catalyst surface showing appreciable improvement in catalyst activity [6,7]. Out of the top-12 proposed biomass-derived

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platform molecules [8], several are fermentation derived and show potential for further upgrading via metal catalyzed hydrogenation and other deoxygenation reactions [4,9]. Most importantly, interests in lignin processing have introduced fermentation derived phenolics [10], which may become potential candidates to act as the platform molecules. For the valorization of such biomass-derived molecules, Ni based catalysts are explored as a viable and cheap option to carry out catalytic transformations including a wide-range of reactions such as hydrogenation, hydrogenolysis and C-H bond activation as shown in Fig. 1 [5,9,11]. However, on performing hydrogenation reaction in aqueous phase, biogenic impurities such as Met and Cys lead to a complete and irreversible deactivation of the Ni surface [5]. While deactivation of the Ni catalyst by S and carbonaceous deposits is a common discussion in catalysis literature, deactivation caused by a biogenic impurity is a relatively new and unexplored phenomenon and requires better understanding. To our knowledge, only one study has experimentally discussed this issue by measuring reactant coverage on the Ni surface in presence of model biogenic impurities (e.g. Met, Cys, Trp, His and Thr) [5]. Few other reports have discussed similar deactivation of Pd, Pt and Ru catalysts [5,12]. However, the deactivation in case of Ni was measured to be more severe as compared to the other metals (Pd and Pt) [5]. Indeed, a detailed comprehensive theoretical basis for the interaction of biogenic impurities with the metal catalyst surface in general and Ni in particular is missing, which needs immediate attention for the development of the integrated process.

An amino acid present with the reactant molecule in a catalytic reaction may interact with the metal surface through the backbone N (amino group) and/or O atoms (carboxylic group). The side chain containing strong binding sites (for example a S atom), may provide purely electronic effect in its interaction with the metal surface. In addition, the orientation, presence of an aromatic ring and length of the side chain are expected to introduce dispersion effects. Bonded interactions of S containing compounds such as alkyl thiols with the metal catalysts have been discussed with DFT calculations in some studies [13,14]. A relatively recent work by Medlin, Janik and co-workers had explored the effect of dispersion interactions of longer chain alkyl thiols in preferential binding to a specific site on the Pd catalyst [15]. In addition, the presence of the aqueous-phase in fermentation-derived systems may affect catalysis at the metal-water interphase by changing the nature of the electronic and dispersive interactions. In general, theoretical studies in the past have focused either on the bonded or non-bonded interactions of amino acids or similar biological molecules with the metal surface [16–22]. However, application to biogenic impurities essentially requires the simultaneous assessment of both types of interactions, which underlines the motivation of this study. For this purpose, utilizing MD simulations, a variety of amino acids with different hydrophobic content were chosen to study dispersive interactions with the Ni surface. The selection included the amino acids (Ala, Cys, Met, Trp, His and Thr) studied in the experiments of Dumesic [5] and Miller's [12] group. In addition, in order to study the side chain specificity on the metal surface, an amino acid with the acidic (Glu) and one with the basic (Lys) side chain were included. The bonded interactions of the S-containing amino acids (Met and Cys) were studied using DFT simulations, calculating energetics for its dissociation to elemental S, leading to complete and irreversible catalyst deactivation as reported in the experimental studies [5].

Altogether, a molecular level catalyst design principle may be explored to counter the deactivation effect of biogenic impurities. Traditional ideas on bimetallic alloy catalyst for example alloying Pd with Au have been explored [6,16]. In the preliminary experiments of Pd-Au bimetallic with Met as the biogenic impurity, no appreciable improvement in the stability of the bimetallic catalyst

was observed [6]. However, in case of the Ni catalyst, Au alloying is known to be instrumental in improving catalyst stability, for example in steam-reforming reaction, by providing weaker binding of carbon [23]. Herein, DFT simulations on Pd-Au bimetallic overlayers and surface alloys have been utilized to understand likely reasons of catalyst deactivation. In contrast to the Pd-Au catalyst, DFT and MD simulations on Ni-Au alloy showed encouraging results, wherein the catalyst may show better performance by providing relatively weaker S and Met binding sites.

2. Computational methods

2.1. MD simulations

MD simulations of amino acids on the metal surface were performed using CHARMM-METAL force field [24] with GPU-accelerated NAMD 2.10 package [25]. The structures of amino acids in their zwitter ionic form having a protonated amino group and deprotonated carboxylic group were used in simulations. The side chains for Lys, Glu and His were modeled in their neutral forms to mimic their natural occurrence form in water at physiological pH. The initial coordinates of Cys-dimer were chosen from bovine serum albumin (first frame of PDB id: 1ao6.pdb) [26]. The amino acids and Cys-dimer were then solvated with mTIP3P waters [27] using *solvate* plugin in VMD [28]. A slab consisting of three atom layers was used to model Ni (111) surface. The metal surface was placed at the bottom of the box and the top layer of the metal surface was denoted by $z = 0$. A non-orthogonal box of $48 \text{ \AA} \times 48 \text{ \AA} \times 47 \text{ \AA}$ was used to model Ni (111) surface. In order to avoid interactions of amino acids and Cys-dimer with their periodic images, an empty space extending up to 100 \AA in the z direction, was included in the simulation cell. In a separate study by Knecht et al. [29], a hybrid combination of experimental, reverse Monte Carlo and MD simulations using CHARMM-METAL force field was employed to compute reaction rates quantitatively. In another study, they used modified LJ parameters to reproduce experimental densities and surface energies of fcc metals at 298 K, eliminating the deviations in surface properties and bulk properties [30]. Since the objective of this study did not include a comparison of structural organization or dynamics of the surface and bulk, LJ parameters as implemented in CHARMM-METAL force field were considered to be a good basis for calculations.

The solvated system was inserted onto the metal surface and the system was energy minimized for 0.5 ns using the conjugate gradient method. Simulations were then performed at NVT conditions with a time step of 1 fs. Langevin thermostat with damping coefficient of 1 ps^{-1} was used to maintain a constant temperature of 300 K. A cut-off distance of 10 \AA was used for van der Waals interactions with a switch distance of 12 \AA , as implemented in NAMD. Particle Mesh Ewald was used to compute long range coulombic interactions with a grid spacing of 1 \AA . Since metal atoms were held fixed in their lattice positions, intra-metal interactions were not taken into account. These values are in accordance to simulation standards with a balance between computational accuracy and speed [31,32].

Fig. S1 shows the stacking of water molecules in two distinct layers above the Ni surface as observed in water runs. In order for the amino acids to interact with the metal surface, it was necessary for amino acid to shed its own hydration waters as well as penetrate the water molecules above the metal surface, which is not a spontaneous process. Hence, a non-equilibrium Steered Molecular Dynamics (SMD) approach was utilized to calculate interaction energies of amino acids on the metal surface. The translational as well as rotational motion in x and y directions was not restrained and the amino acids were allowed to move freely in

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