Ab initio study of ligand dissociation/exchange and the hydrogen production process of the Co(dmgH)$_2$(py)Cl cobaloxime in the acetonitrile-water solvent

Jinfan Chen, Patrick H.-L. Sit[*]

School of Energy and Environment, City University of Hong Kong, Hong Kong Special Administrative Region

ABSTRACT

Density functional theory (DFT) calculations and Car-Parrinello molecular dynamics (CPMD) simulations in the explicit acetonitrile-water solvent were carried out to study the ligand dissociation/exchange process and hydrogen production pathway of a common cobaloxime complex, Co(dmgH)$_2$(py)Cl (py = pyridine). Our results show that the axial Cl$^-$ is readily replaced by a water molecule which is a key step for the subsequent proton transfer in the hydrogen production cycle. Moreover, the py ligand also dissociates readily from the complex at a later stage. The alternate two electrons and two protons addition pathway was identified to be the favorable one for hydrogen production. The rate determining step of the hydrogen production by Co(dmgH)$_2$(py)Cl is the first protonation of the Co ion, which competes with the proton transfer to the O of the side group of the complex.

1. Introduction

The cobaloxime complex, Co(dmgH)$_2$(py)Cl (dmgH = dimethylglyoximate, py = pyridine), has been widely studied as a promising catalyst for hydrogen production in the aqueous environment with high efficiency [1–13]. The structure of Co(dmgH)$_2$(py)Cl has a py and a chloride ligands binding to each side of the planar structure of the prototypical Co(dmgH)$_2$ cobaloxime.

For Co(dmgH)$_2$(py)Cl, as well as many other cobalt-based complexes [14–16], the common reaction steps for H$_2$ generation are believed to include the reduction of the cobalt center from the Co^{III} or Co^{II} state to Co^I. This is followed by protonation to the Co center to form Co^{III}H. One subsequent pathway involves the Co^{III}H hydride reaction in a bimetallic pathway with another Co^{III}H species, or in a monometallic pathway with a proton to produce H$_2$. On the other hand, the Co^{III}H can also be further reduced into Co^{II}H which can also lead to H$_2$ generation in either the bimetallic or the monometallic manner [14,15]. Here the Roman numerals after the Co is the formal oxidation state of the Co ion during the reaction and the H represents the hydride ion bonded to the Co ion. Previous studies have shown that the alternate electron and proton additions pathway is often the more favorable pathway for hydrogen production for Co(dmgH)$_2$(py)Cl in the acetonitrile(AN)-water mixtures, which have been the commonly-used solvent for this class of catalysts [6,7,17].

Py is supposed to be strongly coordinated to the Co center of the Co

(dmgH)$_2$(py)Cl complex. However, during the reaction, the ligand dissociation/exchange can occur, which can significantly affect the catalytic performance of the cobalt complex [3,18–21]. Eisenberg and coworkers [3,18] studied the photocatalytic system with the fluorescein as the photosensitizer and the Co(dmgH)$_2$(py)Cl as the proton reduction catalyst. They found that with triethanolamine (TEOA) as the proton source, the system with the fluorescein connected to the catalyst through the axially coordinated py is less active than the one with separate fluorescein and catalyst. They attributed this to the py exchange process resulting in the less stable integrated system during H$_2$ photogeneration [3,18]. On the other hand, modification on the axial-ligand like the py of the Co(dmgH)$_2$(py)Cl complex can help tune the properties of the complex and is critical in the design of the robust catalytic system where the proton reduction catalysts and the electrode/photosensitizer are connected via the axial-ligands [20,22–24]. Wang et al. [10] studied the effects of the py-based axial-ligands on the photocatalytic hydrogen production properties of the Co(dmgH)$_2$(py)Cl complex in the AN-water solvent and found that the catalyst displays enhanced photocatalytic activities no matter the substituent in the axial py ligand is electron-donating or electron-withdrawing, providing a path to the design of efficient catalysts for hydrogen production [10]. Panagiotopoulos et al. [25] also showed that the performance of the photocatalytic hydrogen production of Co(dmgH)$_2$(py)Cl can be improved by modifying the axial py ligand or through the introduction of TiO$_2$ nanoparticles. In particular, they found that the cobaloxime

complex with the electron-rich substituent in the axial py ligand displays the highest turnover number. They also found that the turnover number increases significantly when TiO_2 nanoparticles was added to the system for the cobaloxime complex with a carboxylic group on the py ligand, which may result from the strong interaction between the cobaloxime and the TiO_2. This leads to the enhanced catalytic properties [25].

Ab initio methods such as DFT can be powerful tools to provide insights into the reaction details and help the design of molecular complexes for hydrogen production [26–34]. The DFT study on the hydrogen production pathways of the $Co(dmgH)_2(py)Cl$ was first reported by Jiang et al. [35], who identified that the H_2 production can occur via the $Co^{III}H$ species in both monometallic and bimetallic pathways, with the former being more energetically favorable. The calculations also displayed the readily protonation of the O−H−O side-group of the complex and the role of the H_2O molecules in assisting the proton transfer to the Co center by lowering the energy barrier of proton transfer significantly [35]. The DFT calculations of another group of common cobaloxime complex, $Co(dmgBF_2)_2$ ($dmgBF_2$ = difluoroboryl-dimethylglyoxime), by Solis et al. [36] and Muckerman et al. [37] showed that the complex is more likely to react via the monometallic pathway on which the electrons and protons are alternatively added and the H_2 is generated by the protonation of the $Co^{II}H$ species. Their studies also showed that at the resting state of Co^{II} there are two axial ligands (solvent molecules) coordinating to the cobalt complexes and one of ligands dissociates at the state of Co^I. Recently, our group carried out ab initio studies on the hydrogen production mechanisms of the $Co(dmgBF_2)_2$ and $Co(dmgH)_2$ complexes in the explicit AN-water solvent [29]. We found that the two complexes are favorably coordinated with one AN and one water molecules as the ligands. The resulting complexes are denoted as $Co(dmgBF_2)_2ANH_2O$ and $Co(dmgH)_2ANH_2O$. Moreover, our results confirmed the favorable alternate electron and proton addition pathway for hydrogen production by the complexes and showed that the solvent molecules, especially the water, play an important role in the hydrogen production process [29].

Design of efficient molecular hydrogen-producing catalysts requires the complete and unbiased understanding of the mechanism of the hydrogen production reactions [14,26,27,38,39]. Despite so many works on the $Co(dmgH)_2(py)Cl$ and other cobalt-based molecular complexes for hydrogen production have been carried out, controversial on the H_2-generation pathway exists and the details of the reactions are still not clear due to the complexity of the reactions. Also, the molecular details of ligand exchange of the molecular complexes and their interaction with other components during the reaction were not well revealed. Building on our earlier simulation work on the cobaloxime complexes of $Co(dmgBF_2)_2$ and $Co(dmgH)_2$ [29], here we perform *ab initio* studies of the hydrogen production process of the $Co(dmgH)_2(py)Cl$ complex in the solvent environment. The structural properties of the complex during the reaction process, in particular the ligand exchange and interaction behavior with the solvent molecules, will be investigated. Similar to the our previous simulations on the cobaloxime complexes [29], the 1-to-1 mole ratio mixing AN-water mixture was chosen as the solvent in this study. The AN and its mixtures with water have been commonly used as the solvents for the hydrogen-production reaction by cobaloximes [6,10,18,40]. The study of $Co(dmgH)_2(py)Cl$ provides in-depth understanding on the catalytic hydrogen production by this complex in the AN-water mixture solvent, which can help to interpret existing studies and predict the behavior of the complex in aqueous environment. Moreover, the results from the simulations of $Co(dmgH)_2(py)Cl$ can provide knowledge on the ligand and solvent dissociation/exchange during the reaction, as well as the effects of axial ligands on catalytic performance.

This article is organized as follows: The computational approach is introduced in Section 2. The results and discussions of this work are in Section 3. The coordination state (ligand dissociation and exchange) of this complex was first discussed. Then the hydrogen production

processes of $Co(dmgH)_2(py)Cl$ were studied via DFT calculations in the gas-phase and via the CPMD simulations in the explicit AN-water solvent. Finally, Section 4 is the summary and conclusions.

2. Simulation details

Plane-wave density functional theory (DFT) calculations in vacuum were performed with the PWscf module of the Quantum Espresso (QE) package [41]. The generalized gradient approximations (GGA) Perdew-Burke-Ernzerhof (PBE) [42] functional and ultrasoft pseudopotentials [43] were used. Gamma-point sampling was adopted in these calculations. The plane-wave kinetic energy cutoff for the soft-part of the wave-functions and the augmented electronic density are 30 Ry and 240 Ry, respectively. For molecular clusters calculations, the molecular clusters were situated in a cubic unit cell of side length 20 Å, which has been tested to be large enough for gamma-point sampling. The Makov-Payne method [44] was used to obtain the total energy to correct for the spurious interactions with the periodic images in the periodic boundary conditions. The NWChem package [45] was used to carry out the localized basis set calculations for comparison. The density functional and the localized basis sets in the NWChem calculations are PBE and 6-31G**, respectively. In the localized basis set calculations of the ligand dissociation/coordination from/to the cobaloxime complex, the basis set superposition error (BSSE) was corrected by the counter-poise method [46]. Moreover, to further confirm the reliability of the PBE calculations, we also compared the results with those from the more expensive B3LYP functional with the NWChem package. The comparisons between the PBE and B3LYP methods are listed in Section S3 in the Supporting Information (SI).

Car-Parrinello molecular dynamics (CPMD) simulations have been widely used as a powerful tool to study the dynamic properties of the many catalytic processes including the reactions of transition metal-based complexes in the explicit liquid environments [29,47–51]. In this work, CPMD simulations of the hydrogen production process of $Co(dmgH)_2(py)Cl$ in the explicit solvent were carried out with the CP module of QE. The initial structure of the AN-water mixture with the mole fraction of AN (x_{AN}) = 0.5 has s 32 acetonitrile and 32 water molecules. This has been fully equilibrated within the *NVT* ensemble for around 10 ns at 300 K with classical molecular dynamics [52], using the GROMACS package [53]. The potential model applied for water is SPC/E, and OPLS/AA for AN [54]. Then, the system with the cobaloxime complex solvated in the AN-water mixture was constructed by replacing six AN and six water molecules with the cobaloxime molecule. The solvent density and the mixing ratio were maintained the same in this procedure. A fictitious electronic mass of 400 a.u. and a time step of 3 a.u. (0.0726 fs) were employed. The functional, the ultrasoft pseudo-potentials and the kinetic energy cutoffs used were the same as those for the molecular cluster calculations in the PWscf calculations. The proton transfer free energy barrier to the Co center in the explicit AN-water solvent was calculated using constrained Car-Parrinello molecular dynamics coupled with thermodynamic integration [29,55,56].

3. Results and discussions

3.1. Density functional theory study of the axial-ligand dissociation and exchange of Co(dmgH)₂(py)Cl in acetonitrile-water mixture

Ligand dissociation and exchange can occur during the catalytic reaction cycle when cobaloximes are solvated in solvents. To study these processes, we calculated the energies of the ligand dissociations from the $Co(dmgH)_2(py)Cl$ complex, as well as interactions between the solvent molecules and the complex in the vacuum (Table 1).

Overall, the results from the plane-wave and the localized basis set methods are in good agreement. The only exception is the relatively large difference in the dissociation energy of Cl^- from $[Co^I(dmgH)_2(py)Cl]^{2-}$ (Reaction 5 in Table 1). This is mainly resulted