Operando XAFS and *AI* MD to characterize Rhodium Clusters in the Catalytic Dehydrogenation of Aminoboranes

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Introduction

The unambiguous assignment of the catalytic species responsible for the controlling the process or the characterization of catalytic reaction pathway is an ongoing challenge in both experimental and computational chemistry. This fundamental insight is critical to help guide development of catalyst materials designed for specific outcomes[1]. Relevant assignments of catalysts or catalyst resting states are even more difficult at the interface between heterogeneous and homogeneous catalysis processes. Often one is left to characterize the catalyst resting state *ex situ* and use chemical intuition to hypothesize potential reaction pathways.

Therefore spectroscopic methods that can be used to identify and follow the fate of the key intermediates formed in a chemical reaction are beneficial to help elucidate mechanistic reaction pathways. We have recently shown that *in-situ* XAFS can be used *operando* to identify the dominant organometallic species formed during the catalyzed release of hydrogen from amine boranes[2]. When coupled with ^{11}B NMR we were able to follow in parallel the decrease in starting material and increase in products containing boron and attempt to correlate the transformation of the corresponding rhodium species. These results lead us to propose a tetrahedral cluster of 4 rhodium atoms stabilized by the presence of multiple boron hydride donor ligands. Based upon the parameters obtained from FEFF analysis of the XAFS spectra collected during the catalytic reaction we narrowed the field to 5 potential structures for the resting state of the catalyst that forms hydrogen from amine boranes[3].

Materials and Methods

Ab initio molecular dynamics (AIMD) calculations were carried out employing Density Functional Theory (DFT) with a gradient corrected functional for exchange and correlation as implemented in the CP2K package. We employ periodic boundary conditions in an 18 Å cubic box which provides at least 5 Å separation between the molecules and the closest contact with its nearest neighbor image. Molecular dynamics (MD) simulations are performed in the NVT ensemble using a well thermalized sample at 300 K. In total over 1 million configuration of the possible resting state were investigated to arrive at a most likely candidate with stoichiometry $Rh_4(BH_2NMe_2)_8^{2+}$.

Results and Discussion

The AIMD simulations from the various starting configurations of the Rh_4 species reveal that for all the structures considered there is significant fluxional behavior leading to large structural rearrangements. For example (i) the Rh_4 cluster isomerizes between a tetrahedral species and a more open one (butterfly) where a single Rh-Rh bond elongates, (ii) terminal BH_2NMe_2 ligands migrate to bridging configurations, (iii) the ligands fluctuate between a species with a close Rh-B contact (ca 2.1-2.2Å) and one where Rh and B are separated by greater than 2.5Å and bridged by a hydride, and (iv) reversible exchange of hydrides form the boron to the rhodium on the Rh_4 cluster. This observed fluxionality indicates that many of the proposed structural features are not independent structures but are in a rapid thermal equilibrium and that a single well defined structure is not appropriate for describing either the relative energetics or spectroscopic properties.

To test the hypothesis that the catalyst resting state is a highly fluxional species we compare the experimental XAFS spectra with the XAFS spectra calculated from the structures obtained by our MD simulation on our lowest energy ensemble of structures. To obtain a real space representation of the XAFS spectra, we calculated the discrete Fourier transform of the structure factor as implemented in the FEFFIT package. The results of this comparison are shown in Figure 1.

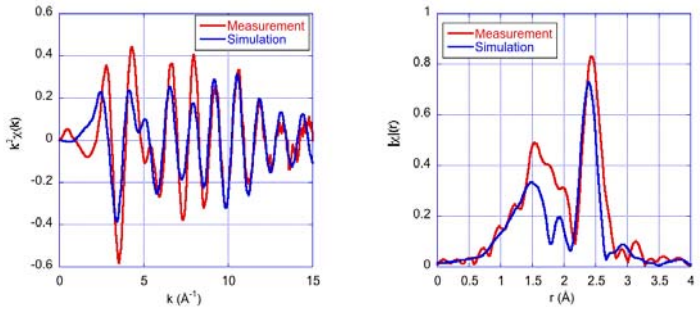

Figure 1. MD-XAFS results for $Rh_4(BH_2NMe_2)_8^{2+}$ a) average $k^2\chi(k)$. c) real space pair distribution, $|\chi|(r)$.

Significance

We have narrowed the field of catalysis resting states from more than 5 structures that fit the geometric constraints of the experimental XAFS spectra to one most likely candidate based upon comparison of relative stabilities determined by AIMD. With this insight we can now postulate a catalytic reaction mechanism for dehydrogenation of amine boranes that are of great interest as potential hydrogen storage materials[4, 5]. These results show how combining *operando* XAFS spectroscopy with *Ab initio* molecular dynamics can be used to obtain fundamental insight into the nature of catalytic reaction pathways.

References

1. Bell, A.T., Gates, B.C., Ray, D., Co-Chairs for *Basic Research Needs: Catalysis for Energy*. Report for US DOE BES (2007)
2. Chen, Y., Fulton, J.F., Linehan, J.C., Autrey, T. *J. Am. Chem. Soc.* 127, 3254 (2005)
3. Fulton, J.F., Linehan, J.C., Autrey, T., Balasubramanian, M., Chen, Y., Szymczak, N.K. *J. Am. Chem. Soc.* 129, 11936 (2007)
4. Peng, B. Chen, J. *Energy Environ. Sci.* 1, 479 (2008)