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Theoretical design of long-life efficient transition metal nanocatalysts towards the activation of C-H bonds at low temperatures

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1. Introduction

In the previous 2017-2018 Narrative Progress Report, we summarized our research on the rhodium (Rh) atomic clusters catalyzed dehydrogenation of ethane. In this 2018-2019 research period, we extended our study to the catalytic activity of Rh clusters bonded to a magnesium oxide (MgO) or O_2 molecule (in progress). In addition, we identified two prescreening tools, the natural bond orbital (NBO) charges and the Wiberg Bond Indexes (WBIs) that correlate quantitatively with the activity of the various catalytic sites of the Rh and iridium (Ir) atomic clusters (Figure 1). These prescreening tools may significantly expedite the global optimization of the Rh and Ir nanocatalysts for the dehydrogenation of ethane and other light alkanes.

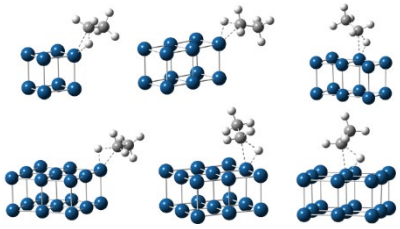

Figure 1. Transitions state (TS) structures of the $TM_n + C_2H_6 \rightarrow H–TM_n–C_2H_5$ (TM=Ir/Rh) reaction taking place at the corner, edge, and/or face center sites.

2. Computational Methods

In The B3LYP hybrid GGA method implemented in Gaussian 09 was used in this study. The D3 empirical dispersion with Becke–Johnson damping (D3BJ) was included in all calculations. In the geometry optimization and vibrational frequency calculations, polarized double-ζ basis sets were used. The LANL2DZ basis set and the LANL2 effective core potential (ECP), augmented with f-type polarization functions, were employed on the Rh atoms. The 6-31G(d) basis sets were employed on the C, H, and O atoms. To further improve the accuracy of the thermochemistry of the Rh_n activated C-H bond cleavage of ethane, single-point energies were calculated using polarized triple-ζ basis sets. The LANL2TZ(f) basis set was employed on the Rh atoms and the 6-311G(d,p) basis sets on the light atoms. The NBO charges and the WBIs were obtained via using the same computational schemes. The NBO analysis was carried out using version 3.1 of the NBO program implemented in Gaussian 09.

3. Results and Discussion

Figures 2-3 demonstrate strong correlations between the NBO charges, WBIs, and the catalytic activities (quantized by the transition state energy) of the Ir and Rh clusters.

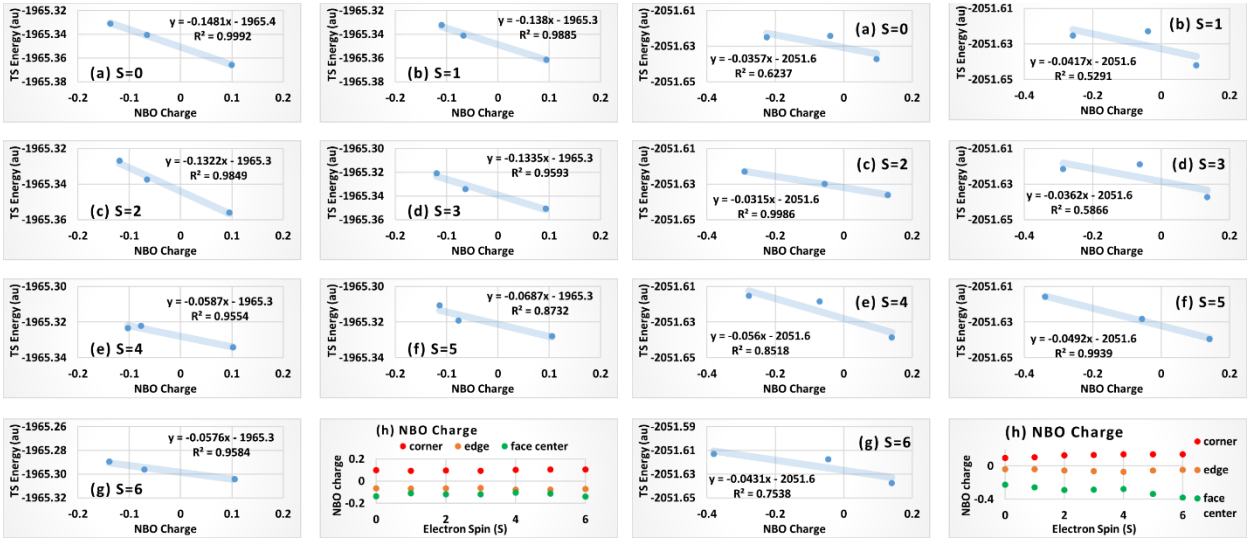

Figure 2. **LEFT HALF:** (a-g: Electron spin S = 0–6) Correlation between the TS energy of the $Ir_{18} + C_2H_6 \rightarrow H–Ir_{18}–C_2H_5$ reaction and the NBO charges of the face center, edge, and corner (from left to right) catalytic sites of Ir_{18}. (h) NBO charges of the three catalytic sites of Ir_{18}. **RIGHT HALF:** Similar analysis for the Rh clusters.

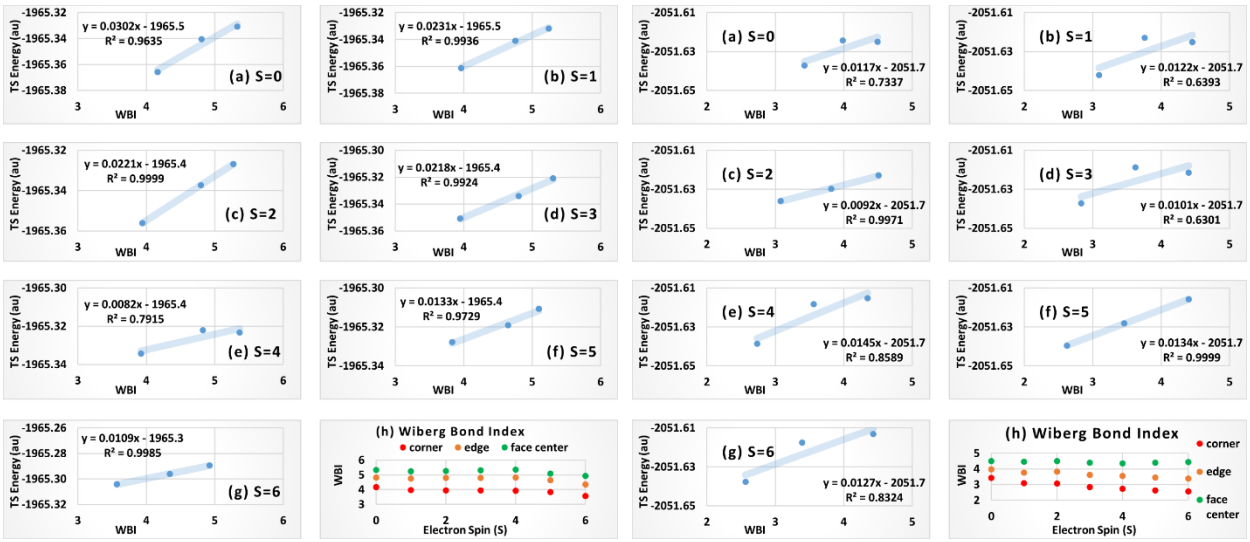

Figure 3 LEFT HALF: (a-g: Electron spin S = 0–6) Correlation between the TS energy of the Ir_{18} + C_2H_6 → H–Ir_{18}–C_2H_5 reaction and the WBIs of the face center, edge, and corner (from left to right) catalytic sites of Ir_{18}. (h) NBO charges of the three catalytic sites of Ir_{18}. **RIGHT HALF:** Similar analysis for the Rh clusters.

In sum, the B3LYP calculations reveal a strong correlation between the NBO charges and the catalytic abilities of the various sites on the Ir and Rh clusters. The more positive the NBO charge, the more active the catalytic site. Similarly, the WBIs are also strong indicators of the activities of different catalytic sites. The lower the WBI, the more active the catalytic site. Compared to the MO visualization and the Mulliken analysis that are basis set dependent and qualitative rather than quantitative, both the NBO charges (Figure 4) and the WBIs are quantitative and virtually independent of the basis sets. The NBO charges and WBIs are expected to provide a reliable means of fast prescreening the best catalytic sites on the Ir, Rh, and potentially other TM clusters for the dehydrogenation of ethane and other light alkanes. This fast and reliable prescreening tool is expected to expedite our future work on the global optimization of the TM catalysts used for the production of ethene and propene at low temperatures.

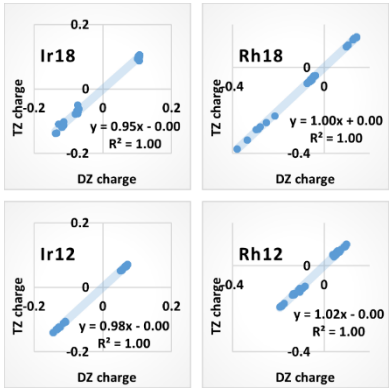

Figure 4. Double-ζ (DZ) vs triple-ζ (TZ) NBO charges of the atoms in the TM_{18} and TM_{12} (TM=Ir, Rh).

4. Research in Progress and Future Plan

We have initiated the study of the catalytic activity of the Rh clusters bonded to MgO for two purposes: One is to estimate the probability of the unwanted migration of the Rh clusters deposited on or partially embedded in the MgO surface. The other is to investigate the effect of MgO on the catalytic activity of the Rh clusters. We have also initiated the study of the catalytic activity of the Rh clusters in an oxygen-rich environment. In the near future, we aim to implement a python program that automates the global optimization of the transition metal nanocatalysts. The prescreening tools we identified for Ir and Rh catalysis, the NBO charges and the WBIs, will be used to expedite this global optimization process as they both strongly correlate with the catalytic activity of the various sites of the Ir and Rh clusters we studied.

5. Impact of the Research on My Career and That of the Students Who Participated

Part of the research conducted in the 9/2018-8/2019 period was presented by undergraduate students at the ACS regional meeting in June 2019 and at the ACS undergraduate research symposium in April 2019. Two research students graduated with a Bachelor's degree in June 2019; one of them is now pursuing a MS degree in chemistry engineering at University of Rochester. Six undergraduate students and I worked on and submitted a research manuscript, titled *Tools for prescreening the most active sites on Ir and Rh clusters toward C-H bond cleavage of ethane: NBO charges and Wiberg bond indexes*, to ACS Omega in August 2019. Part of the content of this manuscript is included in this narrative progress report. ACS PRF donors are acknowledged in the manuscript.