

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

We aim to design long-life transition metal nanocatalysts towards the C-H activation of small alkanes. To achieve this goal, one strategy is to search for thermally stable nanocatalysts with a large enough surface area that bond strongly with their supporting surface. Strong bonding to the surface prevents the nanocatalysts from migration, coalescence, and consequent deactivation. However, larger transition metal nanocatalysts are often less effective than smaller ones because a greater percentage of the atoms in larger clusters are fully coordinated and less active. Therefore, finding the optimal size of the transition metal nanocatalysts is crucial. During the reporting period, we studied the Rh clusters of various sizes and their ability of breaking the C-H bond of ethane. Rh₁₈ clusters with a 3×3×2 cuboid structure are thermally stable and break the C-H bond easily. Moreover, the Rh₁₈ cuboid structure has a sufficiently large bottom surface area of 9 atoms to bond strongly with the supporting surface.

2. Computational Methods

In our previous published research, B3LYP was found reasonably accurate modeling the dehydrogenation of alkanes catalyzed by Pt and Ir clusters and for modeling TiO₂ surface. During this reporting period, we further compared B3LYP with several popular functionals (B2PLYP, B3PW91, PBE0, BLYP, BPW91, PBE, SVWN) for 16 small Rh molecules that contain H, C, O atoms. CCSD(T) calculations were done as the benchmark. In all calculations, the LANL2TZ(f) basis set and the LANL2 pseudo potential were employed on the Rh atoms and the 6-311G(d,p) basis sets on the H, C, and O atoms. The D3 empirical dispersion formulated by Grimme with Becke–Johnson damping was included in the DFT calculations. The errors of the DFT-calculated bond energies (relative to the coupled-cluster results) show significant difference between the various categories of the DFT functionals: the hybrid functionals (19-25 kJ/mol errors) are significantly more accurate than the pure functionals (75-95 kJ/mol errors), which are in turn superior to the SVWN local functional (~200 kJ/mol error). Although the B2PLYP and PBE0 methods slightly outperform the B3LYP method for the test molecules, we decided to continue using the B3LYP method because B2PLYP is computationally expensive and we hope to ensure the methodology consistency of the research for other transition metals (e.g., Pt, Ir) and metal oxides (e.g., TiO₂). In the geometry optimization and vibrational frequency calculations, the LANL2DZ(f) basis set and the LANL2 effective core potential were employed on the Rh atoms, the 6-31G(d) basis sets on the C, H, and O atoms. Single-point energies were calculated using the LANL2TZ(f) basis set for the Rh atoms and the 6-311G(d,p) basis sets for the C, H, and O atoms. The harmonic-oscillator rigid-rotor approximation was made in the vibrational frequency calculations. An extensive search for the reaction paths of Rh_n + C₂H₆ → H–Rh_n–C₂H₅ were then conducted for five different cluster sizes (*n* = 4, 6, 8, 12, 18) in ten different electron spin (*S*) states (*S* = 0–9). Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the transition state (TS) structure connects the desired reactant and product.

3. Results: Rh₆ and Rh₁₈ break C-H bond easily. Rh₁₈ is superior as it bonds strongly to supporting surfaces.

We first conducted global optimization of the Rh_n (*n* = 4, 6, 8, 12, 18) atomic clusters starting from various starting geometries (Figure 1), each in ten different spin states (*S* = 0–9).

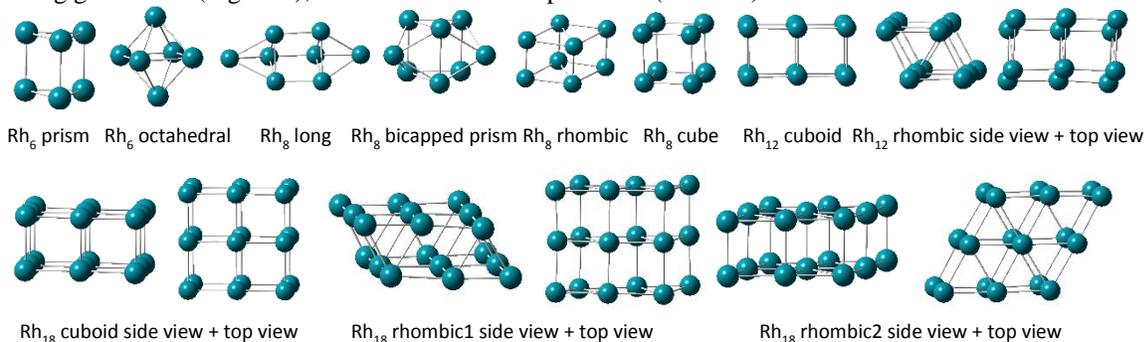


Figure 1. Rh_n (*n* = 6, 8, 12, 18) atomic clusters. Rh₄ tetrahedral and planar structures are not shown.

The global search suggested that Rh₄ tetrahedral (*S* = 3), Rh₆ octahedral (*S* = 3), Rh₈ bicapped prism (*S* = 6), Rh₁₂ cuboid (*S* = 5), Rh₁₈ cuboid (*S* = 1) structures have the lowest energy and are thermally stable.

The potential energy surfaces (PES) of the $\text{Rh}_n + \text{C}_2\text{H}_6 \rightarrow \text{Rh}_n \cdots \text{C}_2\text{H}_6 \rightarrow \text{TS} \rightarrow \text{H-Rh}_n\text{-C}_2\text{H}_5$ reaction paths were calculated for the five cluster-size ($n = 4, 6, 8, 12, 18$) with various shapes, each in ten different spin states ($S = 0-9$). For each cluster size and shape, the reaction paths were calculated on various catalytical sites (e.g., breaking C-H bonds at the corner vs edge site on the Rh_{18} cuboid). A total of 200 PESs have been calculated. The most promising reaction paths for each cluster size are summarized below in Table 1:

Table 1. The size, shape, spin state, and multiplicity of the global minimum of the Rh clusters and their corresponding enthalpy of activation towards the C-H bond cleavage of ethane.

Clusters	Shape	S	M=2S+1	Apparent ΔH^\ddagger (kJ/mol) ^a	Catalytical Site
Rh_4	Tetrahedral	3	7	33	
Rh_6	Octahedral	3	7	-21	
Rh_8	Bicapped Prism	6	13	29	Prism Corner
Rh_{12}	Cuboid	5	11	31	Corner
Rh_{18}	Cuboid	1	3	-10	Corner

^aApparent $\Delta H^\ddagger = H(\text{TS}) - H(\text{Rh}_n) - H(\text{C}_2\text{H}_6)$. It becomes *negative* when the attraction in the $\text{Rh}_n \cdots \text{C}_2\text{H}_6$ complex is negative enough to compensate the positive energy barrier of the $\text{Rh}_n \cdots \text{C}_2\text{H}_6 \rightarrow \text{H-Rh}_n\text{-C}_2\text{H}_5$ reaction.

Both Rh_6 octahedral and Rh_{18} cuboid structures break the C-H bond of ethane easily with a *negative* apparent enthalpy of activation. However, Rh_6 is less ideal because up to only 3 Rh atoms in a Rh_6 octahedral structure can bond to the supporting surface. We expect that Rh_6 clusters migrate and coalesce easily on a supporting surface. Whereas up to 9 Rh atoms in a Rh_{18} cuboid structure can bond with its supporting surface to prevent migration. Figure 2 illustrates the $\text{Rh}_{18} + \text{C}_2\text{H}_6 \rightarrow \text{H-Rh}_{18}\text{-C}_2\text{H}_5$ reaction path in its electronic ground state.

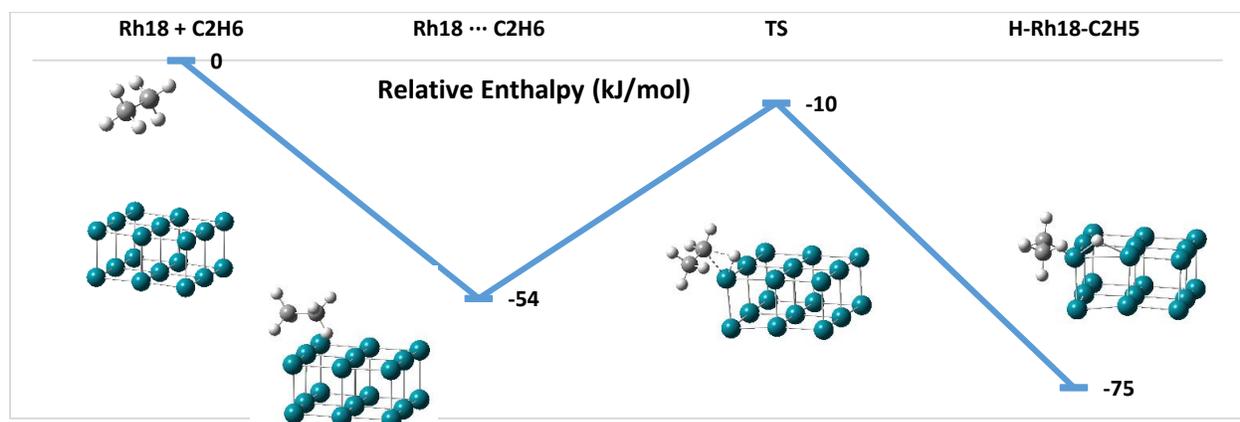


Figure 2. Enthalpy profile of the $\text{Rh}_{18} + \text{C}_2\text{H}_6 \rightarrow \text{H-Rh}_{18}\text{-C}_2\text{H}_5$ reaction in the triplet electronic (ground) state.

The relative Gibbs energies of the four structures in Figure 2 are 0, -29, 10, -51 kJ/mol (from left to right) at the room temperature. The small Gibbs energy of activation (10 kJ/mol) indicates that the Rh_{18} -catalyzed C-H bond breaking reaction of ethane may proceed fast even at the room temperature. The bottom 9 Rh atoms in the Rh_{18} cuboid structure may bond with a supporting surface strongly and thus effectively prevent the migration, coalescence, and deactivation of the Rh_{18} clusters at or near the room temperature.

4. Research in Progress and Future Plan

We are currently investigating the second H-elimination of ethane on the Rh_{18} cuboid structure, $\text{H-Rh}_{18}\text{-C}_2\text{H}_5 \rightarrow (\text{H})_2\text{-Rh}_{18}\text{-C}_2\text{H}_4$, followed by oxygen being adsorbed on the Rh_{18} cluster surface and taking away the two H atoms. We will then study the catalytic activity and stability of the surface-supported Rh_{18} clusters and Ir_{18} clusters. Ir_{18} clusters were previously found to be thermally stable and break the C-H bond of ethane easily.

5. Impact of the research on my career and that of the students who participated

The research conducted in the reporting period has been presented by undergraduate students at the ACS national meeting in March 2018, the ACS undergraduate research symposium and a university symposium in May. Two research students graduated with a BS degree and landed a job in a chemistry or related company; one will continue pursuing a BA degree in chemistry with a teaching certificate. We are working on a manuscript and expect to submit it this winter. We also aim to extend this project and submit a NSF CAT proposal in September 2019.