Cyclohexane dehydrogenation catalyst design based on spin polarization effects

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Abstract

We investigate and discuss spin polarization effects on cyclohexane (C_6H_{12}) dehydrogenation using a Ni atom as a test catalyst, by performing total energy calculations based on the density functional theory (DFT). We compare the results with those of the well known catalyst Pt. We consider the process where cyclohexane approaches a transition metal M (M: Ni and Pt), and determine the reaction paths from the calculated potential energy surfaces (PESs) for singlet cyclohexane/M and triplet cyclohexane/Ni systems. Unlike the singlet cyclohexane/Ni, no energy is required to separate cyclohexyl intermediate (C_6H_{11}) from the H–Ni system for the triplet cyclohexane/Ni. Our results suggest that the catalytic reactivity of spin-polarized Ni becomes close to that of Pt, which is considered to be, up to now, the best catalyst for cyclohexane dehydrogenation.

1. Introduction

Recently, from an environmental viewpoint, much attention has been focused on cyclohexane (C_6H_{12}) as one of the hydrogen storage materials for fuel-cell vehicles [1–3]. Since cyclohexane is in the liquid state under room temperature and pressure, we can use it to store and supply hydrogen in a stable form as a hydrogen carrier. Moreover, cyclohexane has a higher storage performance than the other candidates, e.g., compressed hydrogen, liquid hydrogen, hydrogen storing metal alloys and carbon materials. Its hydrogen storage densities, based on both weight and volume (7.2 wt%, 56.0 kg H_2/m^3 from $C_6H_{12} \rightarrow C_6H_6 + 3H_2$), are equivalent to or higher than those (6.5 wt%, 62.0 kg H_2/m^3) targeted by the Department of Energy (DOE), USA. Noble metal catalysts, e.g., platinum, are required at high temperatures ($\approx$573 K) in order to dehydrogenate cyclohexane efficiently. Thus, designing alternative

catalysts with lower cost and higher reactivity than platinum is important and necessary in order to use cyclohexane realistically as a hydrogen storage–supply medium.

It has been found that cyclohexane is adsorbed on metal surfaces in a chair-like configuration which is the stable configuration (D_{3d} symmetry) in the gas phase [4–7]. However, the cyclohexane dehydrogenation process and the identification of the intermediates are still not understood, especially from a microscopic viewpoint.

The choice of nickel is mainly due to its availability and reasonable cost, as compared with noble metals, e.g., platinum. It is also well known that nickel is ferromagnetic. It has been found that the magnetic moments can be enhanced at a nickel surface relative to its bulk, and that molecular adsorbates are able to reduce the magnetic ordering of nickel, particularly in the bonding region between adsorbate and substrate [8–10].

Taking the above background into consideration as a preliminary step, we use just one transition metal atom as a catalyst in order to consider microscopically the interaction between cyclohexane and the transition metal catalyst. Our previous studies [11, 12] indicate that the cyclohexane dehydrogenation process essentially depends on the properties of the transition metal element, i.e., electrons of the outermost core and valence orbitals of the transition metal atom. From this viewpoint, we believe that the results in the present study represent a qualitative explanation for the interaction between cyclohexane and the transition metal catalyst. We have already investigated the cyclohexane dehydrogenation with a Pt atom [11] and Pt_3 cluster [13], and confirmed that the cyclohexane/Pt_3 system supported the cyclohexane dehydrogenation process for the cyclohexane/Pt system.

Here, we investigate spin polarization effects on the first C–H bond cleavage in cyclohexane interacting with Ni, leading to the formation of cyclohexyl intermediate (C_6H_{11}) as a key elementary step for the cyclohexane dehydrogenation process, as compared with the non-spin-polarized system using Pt. The present study aims to make a first step toward a better understanding of how reaction with a spin-polarized metal catalyst can induce the cyclohexane dehydrogenation process.

2. Model and method

In the present study, we perform total energy calculations, based on the density functional theory (DFT) [14, 15], to investigate cyclohexane interaction with a transition metal atom M (M: Ni and Pt). We attach the M to one of the axial-H atoms of the cyclohexane in order to form the C–(axial-H)$\ldots$M configuration, where the structure of the cyclohexane is optimized to have D_{3d} symmetry.

Figure 1 shows the cyclohexane/M system considered in the present calculations. We use the equilibrium position for the cyclohexane/M as the initial state, relaxing only the (axial-H)–C–(equatorial-H) angle θ. For the first C–H bond cleavage in the cyclohexane/M, we vary the C–M distance z and the C–(axial-H) distance r.

We perform DFT-based total energy calculations using the Gaussian98 programs [16], adopting Becke three-parameter hybrid functionals [17], the Perdew–Wang gradient-corrected correlation functional [18] and Hay–Wadt basis sets [19]. For the triplet cyclohexane/Ni, the spin contamination can be negligible because all of the calculated values of $\langle S^2 \rangle$ are 2.00.

3. Results and discussion

We calculated the potential energy surfaces (PESs) for singlet cyclohexane/M (M: Ni and Pt) and triplet cyclohexane/Ni systems, as functions of z and r, and determined the reaction paths along the potential minima on the PESs. From the reaction paths, we considered the cyclohexane dehydrogenation process. The C–H bond dissociation processes of the
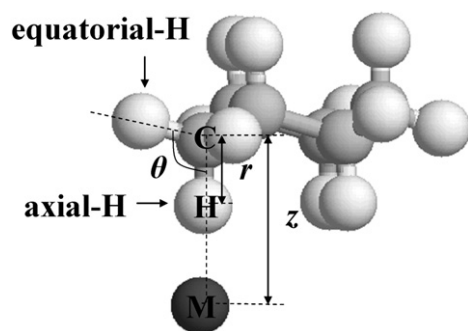
Figure 1. Cyclohexane/M (M: Ni and Pt) system in the present calculations. For the first C–H bond cleavage in the cyclohexane/M, we vary the C–M distance z and the C–(axial-H) distance r, relaxing only the (axial-H)–C–(equatorial-H) angle θ.
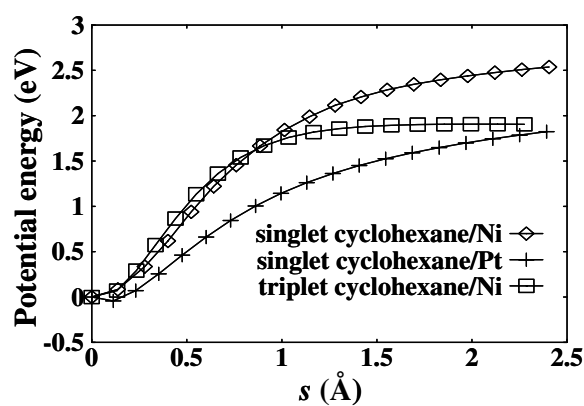

Figure 2. Calculated potential energy curves for singlet cyclohexane/M (M: Ni and Pt) and triplet cyclohexane/Ni systems, as a function of reaction coordinate s. At $s = 0$ Å, cyclohexane adsorbs on the M. As s increases, the M draws the H atom of the cyclohexane and then cyclohexyl intermediate (C_6H_{11}) separates from the H–M system. The origins of the three curves correspond to the total energies of the equilibrium positions for the three systems, respectively.

cyclohexane for the three systems are almost the same. Upon interacting with the M, the M draws an H atom from the cyclohexane, forming an H–M bond. With the C–H bond broken, cyclohexyl intermediate (C_6H_{11}) separates from the M. Figure 2 shows the calculated potential energy curves for the three systems, as a function of reaction coordinate s. At $s = 0$ Å, cyclohexane adsorbs on the M. As s increases, the M draws the H atom of the cyclohexane and then the cyclohexyl separates from the H–M system. In figure 2, Pt exhibits the highest reactivity. Unlike the singlet cyclohexane/Ni, no energy is required to separate the cyclohexyl from the H–Ni system for the triplet cyclohexane/Ni. The phenomenon is due to the repulsion between up-spin electrons, resulting from the up-spin electron transfer from the triplet Ni atom to the singlet C atom in the considered C–(axial-H) . . . Ni [20]. It indicates that the magnetic properties of Ni can be favourably utilized for cyclohexane dehydrogenation.

The magnetic moments [21–23] of the enhanced Ni clusters are close to that (2.00 μ_B/atom) of the triplet Ni atom. As for the extended Pt clusters possessing no net magnetic moment, the singlet systems can be applied. Therefore, the results of figure 2 suggest that the catalytic reactivity of the Ni nano-catalyst becomes close to that of Pt.

4. Conclusion

We investigated spin polarization effects on cyclohexane dehydrogenation using a Ni atom as a test catalyst, by performing DFT-based total energy calculations. We compare the results with those of the well known catalyst Pt. Cyclohexane is initially adsorbed on M (M: Ni and Pt), and then becomes dehydrogenated, i.e., the axial-H atom of the cyclohexane is extracted toward the M. Unlike the singlet cyclohexane/Ni system, no energy is required to separate cyclohexyl intermediate (C_6H_{11}) from the H–Ni system for the triplet cyclohexane/Ni system. Our results suggest that the catalytic reactivity of spin-polarized Ni becomes close to that of Pt, which is considered to be, up to now, the best catalyst for cyclohexane dehydrogenation.

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