Cyclohexane Dehydrogenation Process Design Using Ni
- Spin Polarization Effects -

Muneyuki Tsuda
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

Wilson Agerico Diño
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan,
Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan, and
Physics Department, De La Salle University, Taft Ave., Manila 1004, Philippines

Susumu Watanabe, Hiroshi Nakanishi, and Hideaki Kasai*
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan.
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We investigate and discuss spin polarization effects on cyclohexane (C$_6$H$_{12}$) dehydrogenation with a Ni atom, by performing total energy calculations based on the density functional theory (DFT). We consider the process where cyclohexane approaches the Ni atom, and determine the reaction paths from the calculated potential energy surfaces (PESs) for singlet and triplet systems. The C-H bond dissociation processes of the cyclohexane for both singlet and triplet systems are almost the same. After interacting with the Ni atom, the Ni atom draws an H atom from the cyclohexane, and an H-Ni bond is formed. With the C-H bond broken, cyclohexyl intermediate (C$_6$H$_{11}$) separates from the Ni atom. For the triplet system, however, no energy is required to separate the cyclohexyl from the H-Ni system due to the repulsion between up-spin electrons, resulting from the up-spin electron transfer from the Ni atom to the C atom. Therefore, it indicates that the magnetic properties of the Ni atom are favorable for the cyclohexane dehydrogenation. [DOI: 10.1380/ejssnt.2004.200]

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Recently, from an environmental viewpoint, much attention has been focused on cyclohexane (C$_6$H$_{12}$) 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 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 kgH$_2$/m$^3$ from C$_6$H$_{12}$ $\rightarrow$ C$_6$H$_6$ + 3H$_2$), are equivalent or higher than those (6.5 wt%, 62.0 kgH$_2$/m$^3$) targeted by the Department of Energy (DOE), USA. Noble metal catalysts, e.g., platinum, are required at high temperatures (≈573 K) in order to dehydrogenate cyclohexane efficiently.

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, we use just one Ni atom as a catalyst in order to consider microscopically the interaction between cyclohexane and the Ni catalyst. Our previous studies [11, 12] indicate that the cyclohexane dehydrogenation process essentially depends on the properties of a transition metal atom, 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 Ni catalyst. This cyclohexane dehydrogenation process by the cyclohexane/Ni system may be applied to, e.g., the interaction of cyclohexane with nano-clusters or...

FIG. 1: Cyclohexane/Ni system in the present calculations. For the first C-H bond cleavage in the cyclohexane/Ni, we vary the C-Ni distance z and the C-(axial-H) distance r, relaxing only the (axial-H)-C-(equatorial-H) angle $\theta$.  

*Corresponding author: kasai@dyn.ap.eng.osaka-u.ac.jp
TABLE I: Total energies of cyclohexane/Ni systems and calculated values of \(< S^2 >\) at the initial states in the present calculations, as a function of multiplicity of the system.

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (eV)</td>
<td>-11020.64</td>
<td>-11021.97</td>
<td>-11017.59</td>
<td>-11011.16</td>
<td>-11001.83</td>
</tr>
<tr>
<td>(&lt; S^2 &gt;)</td>
<td>0.00</td>
<td>2.00</td>
<td>6.00</td>
<td>12.00</td>
<td>20.00</td>
</tr>
</tbody>
</table>

FIG. 2: Calculated potential energy curves for singlet and triplet systems, as a function of reaction coordinate \(s\). The origins of the two curves correspond to the total energies of the equilibrium positions for the singlet and triplet systems, respectively. Selected bond distances in Å.

defects such as step-edges on the surfaces. 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 a Ni atom, leading to the formation of cyclohexyl intermediate (C\(_6\)H\(_{11}\)) as a key elementary step for the cyclohexane dehydrogenation process.

In the present study, we perform total energy calculations, based on the density functional theory (DFT) [14, 15], to investigate cyclohexane interaction with a Ni atom. We attach the Ni atom to one of the axial-H atoms of the cyclohexane in order to form the C-(axial-H)...Ni configuration, where the structure of the cyclohexane is optimized to have D\(_3d\) symmetry.

We optimized the structure of cyclohexyl intermediate (C\(_6\)H\(_{11}\)) partially and fully to have C\(_s\) symmetry. For the former, we removed one axial-H atom from the cyclohexane and performed the structural optimization for the cyclohexyl, varying only the (removed axial-H)-C-(equatorial-H) angle. We found that the total energy of the partially optimized cyclohexyl was more than that of the fully optimized one by 0.09 eV. Nevertheless, we believe that the partially optimized cyclohexyl is realistic enough to give the qualitative properties.

Figure 1 shows the cyclohexane/Ni system considered in the present calculations. We use the equilibrium position for the cyclohexane/Ni as the initial state, relaxing only the (axial-H)-C-(equatorial-H) angle \(\theta\). Table 1 shows the total energies of the cyclohexane/Ni and the calculated values of \(< S^2 >\) at the initial states in the present calculations, as a function of multiplicity of the system. The ground state of the system is the triplet state with a singlet-triplet energy difference of 1.33 eV. For the first C-H bond cleavage in the cyclohexane/Ni, we vary the C-Ni distance \(z\) and the C-(axial-H) distance \(r\).

We perform DFT-based total energy calculations using the Gaussian98 programs [16], adopting Becke
FIG. 3: Variations of the angle $\theta$ for the singlet and triplet systems, as a function of $s$. Selected angles in degree.

We calculated the potential energy surfaces (PESs) for singlet and triplet 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 cyclohexane dehydrogenation process. The C-H bond dissociation processes of the cyclohexane for both singlet and triplet systems are almost the same. Upon interacting with a Ni atom, the Ni atom draws an H atom from the cyclohexane, forming an H-Ni bond. With the C-H bond broken, cyclohexyl intermediate (C$_6$H$_{11}$) separates from the Ni atom. Figure 2 shows the calculated potential energy curves for the singlet and triplet systems, as a function of reaction coordinate $s$. For the triplet system, no energy is required to separate the cyclohexyl from the H-Ni system. Figure 3 shows the variations of the angle $\theta$ for the singlet and triplet systems, as a function of $s$. The value of $\theta$ decreases as $s$ increases. The result indicates that the structure of the cyclohexyl changes from sp$^3$-like bonding of -C-H$_2$ to sp$^2$-like bonding of -C-H in order to take a more stable structure due to the removal of the H atom from the cyclohexane. Figure 4 shows the variations of the total atomic charges of the C, H and Ni atoms in the considered C-(axial-H)...Ni for the singlet system according to the Mulliken population analysis [22], as a function of $s$. When $s$ is less than 0.5 Å in Fig. 4, at which the C-H bond initially breaks, the H charge decreases, on the other hand, the C and Ni charges increase. Thus, electron transfer from the C and Ni atoms to the H atom occurs in this region. This indicates that in breaking the C-H bond of the cyclohexane, the back-donation to the C-H anti-bonding $\sigma^*$ orbital dominates over the donation from the C-H bonding $\sigma$ orbital for the singlet system. Figure 5 shows the same as Fig. 4, but for the triplet system. When $s$ is less than 0.5 Å in Fig. 5, the H and Ni charges decrease, on the other hand, the C charge increases. Thus, electron transfer from the C atom to the H and Ni atoms occurs in this region. This indicates that in breaking the C-H bond of the cyclohexane, the donation from the C-H bonding $\sigma$ orbital dominates over the back-donation to the C-H anti-bonding $\sigma^*$ orbital for the triplet system. The results of Figs. 4 and 5 depend on the difference of the equilibrium positions for the singlet and triplet systems at the initial states (Fig. 2). Inset of Fig. 5 shows the variations of the spin densities of the C, H and Ni atoms in the considered C-(axial-H)...Ni for the triplet system according to the Mulliken population analysis, as a function of $s$. At the initial state $s = 0$ Å, the spin density of the Ni atom is almost 2. This indicates that the cyclohexane adsorbate does not affect largely the Ni atom. As the reaction proceeds, up-spin electron transfer from the Ni atom to the C atom occurs. Because of the repulsion between the up-spin electrons of the C and Ni atoms [23], no energy requires for separating the cyclohexyl (Fig. 2). Therefore, this indicates that using the triplet Ni atom is favorable for the cyclohexane dehydrogenation, as compared with the singlet one. Meanwhile, the attenuation of the spin density of the spin-polarized...
FIG. 4: Variations of the total atomic charges of the C, H and Ni atoms in the considered C-(axial-H)...Ni for the singlet system according to the Mulliken population analysis [22], as a function of $s$.

FIG. 5: Same as Fig. 4, but for the triplet system. Inset shows that variations of the spin densities of the C, H and Ni atoms in the considered C-(axial-H)...Ni for the triplet system according to the Mulliken population analysis, as a function of $s$.

Ni atom means that it is not the cyclohexane adsorbate but the separating cyclohexyl that reduces the magnetic ordering of the Ni atom.

We have already considered the quintet cyclohexane/Ni system. However, energy is required to separate the cyclohexyl intermediate ($C_6H_{11}$) as well as the singlet one. We have also investigated the cyclohexane dehydrogenation with a Ni$_3$ cluster, and confirmed that the cyclohexane/Ni$_3$ system favors the energyless separation of the cyclohexyl from the Ni cluster, which has the magnetic moments of ca. 2$\mu_B$/atom. Therefore, our results in this paper may be applied to the realistic Ni clusters, which have the magnetic moments of ca. 2$\mu_B$/atom [24–26].

In conclusion, we investigated spin polarization effects on cyclohexane dehydrogenation with a Ni atom, by performing DFT-based total energy calculations. We suggest that cyclohexane is initially adsorbed on Ni, and then becomes dehydrogenated, i.e., the axial-H atom of the cyclohexane is extracted toward the Ni. As a result, the cyclohexane dehydrogenation processes for both singlet and triplet systems are almost the same. For the triplet system, however, no energy is required to separate the cyclohexyl intermediate ($C_6H_{11}$) from the H-Ni system because of the repulsion between up-spin electrons, resulting from the up-spin electron transfer from the Ni atom to the cyclohexyl. Our results suggest that the magnetic properties of Ni can be favorably utilized for cyclohexane dehydrogenation.

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[23] The electron density in the region involving two up-spin electrons is low. Therefore, the antibonding state is preferred. We called this state "repulsion".