What Activates the Nitrogen Molecule in Ammonia Synthesis Using Supported Metal Catalysts? A Quantum-Chemical Model Study

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The N-N bond breaking of the N$_2$ molecule on a metal surface is the key process in the ammonia synthesis using heterogeneous catalysts. Herein we discuss electronic factors in the bond cleavage on the basis of electronic-structure calculations. It is shown that the hydrogenation of the end-on coordinated N$_2$ molecule may play an important role, which may be accompanied by electron transfer from the catalyst to N$_2$.

Keywords: Electronic-structure calculations, Ammonia synthesis, Catalysis, Supported metal catalyst, Surface adsorption

1 Introduction

Concerned with the ammonia synthesis from the H$_2$ and N$_2$ gases using supported metal catalysts, it has been believed that the N-N bond breaking of the N$_2$ molecule is the rate-determining step [1]. In the process, electron transfer from the catalyst to N$_2$ has been suggested as a key factor accelerating the activation process of the substrate [2].

In this paper, we study electronic factors activating the N-N triple bond of N$_2$ by using density functional theory (DFT) calculations. This study was motivated through the two notions: (1) the electron-attached state of N$_2$ is very unstable [3] so that the electron injection from a catalyst to N$_2$ should be energetically unfavorable even on the catalyst surface, and (2) many hydrogen atoms (or molecules) may play a role in the reaction condition because H$_2$ is chemically active enough to cause "catalyst poisoning" to the MgO-supported Ru catalyst [4].

2 Computational Method

The metal(M)-N$_2$ interaction was investigated using the DFT(M06-2X) method implemented in Gaussian09 [5]. The present molecular models are shown in Figure 1. We used the effective core potential and its valence basis set for metal atoms, while the 6-31G** basis set was used for N and H. In the hydrogenated systems, the molecular charge was set to zero in order to mimic the hydrogen transfer. This process...
is expected to occur on the catalyst surface in the ammonia synthesis from N₂ and H₂. We think that this modeling should be reasonable because our separate supercell calculations on the N₂ adsorption and the H₂ adsorption on the MgO-supported Ru nano particles show that the chemisorption of H₂ is much faster than that of N₂. The supercell calculation was carried out using the MaterialsStudio/CASTEP code [6] at the DFT (PBE)-based first-principles molecular dynamics (FPMD) where the ultrasoft pseudo potential was used and the wave functions were described by the plane wave basis set. Its energy cutoff was determined by specifying the "Express" option in the software. In this implementation, only the Γ point was included in the k space. The catalyst model was prepared through partial optimization of 8Å×8Å×8Å cube-like Ru nano cluster (using the "Nanocluster" option of MaterialsStudio/Visualizer [6]) adsorbed on the MgO(111) surface whose geometry was fixed to that of the single crystal. The gas sorption was simulated at 3000 K at the fixed geometry of the Ru+MgO catalyst where the compressed gas model [7] was applied.

3 Results and Discussion

We performed DFT calculations of the N₂ coordination onto the Na, Cs, Cu, Ag, and Au atoms in order to investigate important electronic factors in activation of N₂. These models were chosen because each metal atom (M) is expected to donate one electron to N₂ upon coordination. This expectation seems reasonable because of the low ionization energies (IE) of the metal atoms: for example, the reported IE value for the Cs atom is only 3.894 eV [8]. As mentioned in the Introduction, electron transfer from metal to N₂ has been considered in the literature as the most important factor in the ammonia synthesis [2].

Table 1. Important geometries and electronic parameters of the models in Figure 1.

<table>
<thead>
<tr>
<th>M atom</th>
<th>M+N₂</th>
<th>M+N₂+H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-N distance (Å)</td>
<td>ν_N-N (cm⁻¹)</td>
</tr>
<tr>
<td>None</td>
<td>1.098</td>
<td>2537</td>
</tr>
<tr>
<td>Na</td>
<td>1.099</td>
<td>2540</td>
</tr>
<tr>
<td>Cs</td>
<td>1.099</td>
<td>2546</td>
</tr>
<tr>
<td>Cu</td>
<td>1.099</td>
<td>2531</td>
</tr>
<tr>
<td>Ag</td>
<td>1.099</td>
<td>2530</td>
</tr>
<tr>
<td>Au</td>
<td>1.099</td>
<td>2537</td>
</tr>
</tbody>
</table>

Figure 1 and Table 1 show some structural and electronic features of the M+N₂ system at the optimized geometry. The following simulation results indicate that N₂ is not activated upon coordination onto the metal atoms: (i) the N₂ coordination on M is found to be very weak as seen in the long M-N distances (longer than 3.2 Å). (ii) The optimized N-N distance is equal to that of the isolated N₂ molecule. (iii) The vibrational frequencies for the N-N stretching in the five complexes and the isolated N₂ molecule are within the range of 2530–2546 cm⁻¹. In addition, (iv) the calculated Mulliken charges on the M atoms were nearly zero. (e.g., −0.02 e for Cs). It is surprising that N₂ does not accept any electrons even in the coordination onto Cs.

Since N₂ is not activated upon coordination onto M, it seems necessary to explore another factor of the N₂ activation. In ammonia synthesis using the N₂ and H₂ gases, many hydrogen atoms are considered to exist on the catalyst surface. This suggests that the H atom may participate in the activation. The influence of the hydrogenation (attachment of the neutral H atom) is studied for the complexes shown in the bottom column of Figure 1. The calculation shows that the N-N distance upon hydrogenation is appreciably elongated to 1.20–1.25 Å. This indicates that the N₂ molecule is activated upon coordination. The calculated vibrational frequencies for the N-N stretching are consistent with the weakening of the N-N bond. The calculated M-N distances indicated appreciable enhancement of the M-N interaction after hydrogenation. In the Cs+NNH system, the net charge on Cs was +0.60, indicating that electron transfer to the NNH moiety is also important. Since the N-N distance and the N-N stretching frequency in the isolated NNH molecule are 1.173 Å and 1973 cm⁻¹, these results suggest that the M-N interaction additionally activates the N₂ molecule.
In parallel with the M+N 2/M+N2+H model calculations, we have been carrying out FPMD calculations on MgO-supported Ru nano cluster (see Figure 2). In this simulation, we include the N 2 molecules to the systems with the hydrated catalyst surface. So far we have been successful to reproduce the formation of one ammonia molecule as shown in Figure 2. In the simulation, the N-N bond breaking was initiated by hydrogenation of N2. This feature is consistent with the present model calculations using the metal atoms discussed above. For further information, extensive FPMD simulations are in progress and will be reported in our future publications.

4 Summary and Conclusions

We have reported electronic structure calculations investigating important chemical factors for N2 activation in the ammonia synthesis. Our simulation results suggest that hydrogenation of N2 on the surface of ammonia synthesis catalysts and electron injection into N2 are the key factors in this important catalytic reaction.

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References