

AB INITIO MOLECULAR ORBITAL CALCULATION FOR THE ANALYSIS OF CARBON/NITROGEN OXIDE REACTION

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Introduction

The reduction of nitrogen oxide by carbon and the N_2 formation from this reaction have been widely investigated in relation to the NO_x and/or N_2O emission during coal combustion. In addition to these experimental approaches, molecular orbital (MO) theory can be very helpful for the understanding of reaction mechanism. Previously, we analyzed this reaction by using a semi-empirical MO theory and we found that the semi-empirical approach sometimes gave chemically unreasonable results [1]. Here, in order to obtain more accurate and reliable calculation results, we have applied an *ab initio* MO theory to the simulation of the chemisorption of NO and N_2O molecules on carbon surface and the subsequent reduction of these gas molecules by carbon.

Calculation Method

The Gaussian 94 package [2] was used for *ab initio* molecular orbital calculation. For simplicity, several single layers of polyaromatic compounds with different sizes were employed as models for carbon. A single NO or N_2O molecule was put at a distance of 0.13 ~ 0.15 nm from the unsaturated edge plane of the models. Then the MO calculation of the whole system including both the model carbon and the gas molecule was made. We employed UHF (unrestricted Hartree-Fock) method with the basis set of 3-21G(d) for geometric optimization, followed by density functional method using the B3LYP functional with the basis set of 6-31G(d) for single point energy calculation.

Results and Discussion

We put NO molecule near zigzag site of the model in the following three ways (Fig. 1); N-down, O-down and side-on. Fig. 2 shows the structure of the surface nitrogen complexes created by the chemisorption in the simulation, together with the heat of adsorption for each species. The N-down approach is more thermally favorable than the O-down one. Through the side-on approach, the most favorable complex (model c) is formed on zigzag site, where both N and O atoms are chemically bonded to edge carbon atoms.

To elucidate the N_2 formation route from the surface nitrogen complexes, we tried to put one more molecule of NO on the N atom of the chemisorbed species similar to model c. The MO calculation for such system resulted in the formation of C(NNO) surface species (model d in Figure 3), where the value of the atomic bond population (a measure of bond strength) for each bond is indicated. The bond population of N-O is much lower than those of the other bonds. The breakage of the N-O bond would be, therefore, easy. In

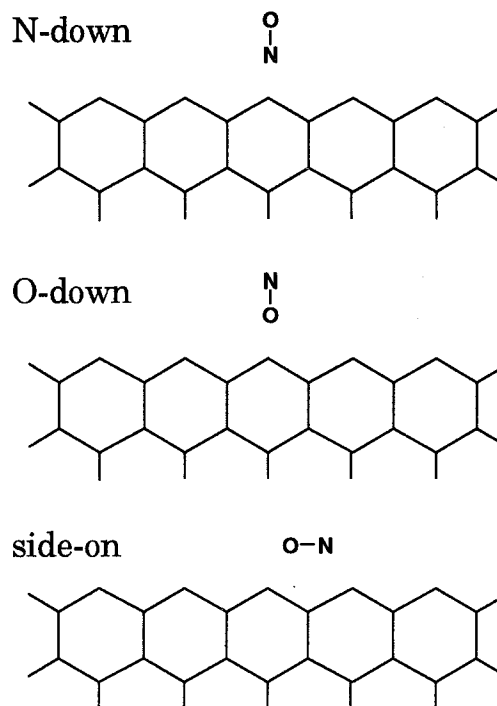


Figure 1. N-down, O-down and side-on modes of NO approach toward zigzag sites.

order to estimate the bond strength of C(NN) species after such bond breakage, we made the optimized calculation for a linear C(NN) species between two C(O)'s. The resultant optimized structure and the values of atomic bond population are shown in Figure 4 (model e). The linearity of C(NN) was kept even after the optimization. It should be noted that N-N bond has a large bond population (1.39), but the value for C-N bond is very small (0.15). Such small atomic bond population would lead to easy desorption of N_2 from model e due to the bond breakage of C-N. Thus, we can expect N_2 formation from the C(NNO) species when once the species has a structure such as model e due to the bond breakage of N-O. A similar analysis was done for the N_2 formation either from the reaction of pyridinic nitrogen with NO or from two neighboring C(N) species on zigzag site. It was found that such N_2 formation is not easy to take place.

The MO calculation was carried out for the carbon/ N_2O reaction. As a result, N-down mode produced unstable C(NNO) surface species, while O-down and side-on ones

led to the release of N_2 gas to leave O atom bonded to edge C atom. The N_2 release process can be expressed by the following equation; $C() + N_2O \rightarrow C(O) + N_2$, where $C()$ and $C(O)$ correspond to free site and surface oxygen complex, respectively. This equation has been proposed so far by many researchers and very recently we have experimen-

tally confirmed that N_2 molecule is mainly formed from a single N_2O molecule during its reaction with carbon [3]. We simulated this experimental finding by the present MO calculation.

In conclusion, the present study demonstrated how an *ab initio* MO theory is useful for the understanding of reaction mechanism even for a very complicated system such as C-NO and C- N_2O reactions.

References

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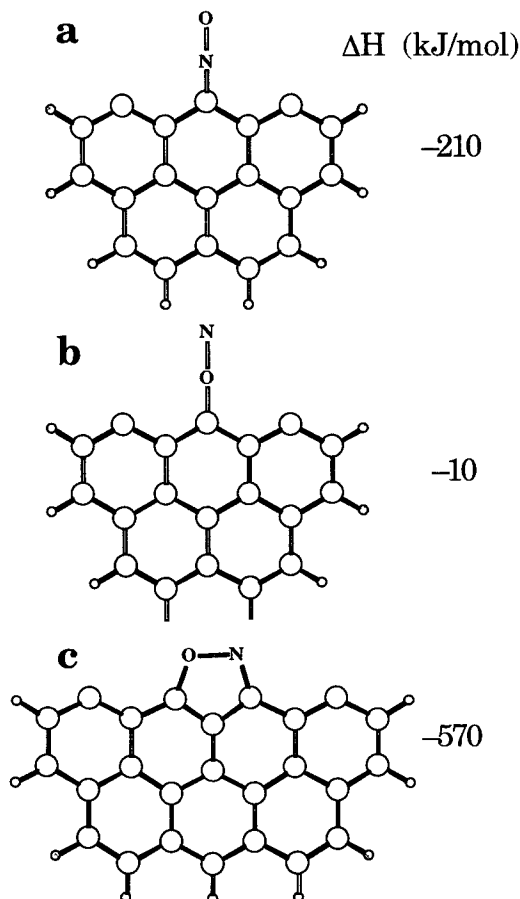


Figure 2. Surface nitrogen complexes formed by NO adsorption on the zigzag site in N- and O-down and side-on modes.

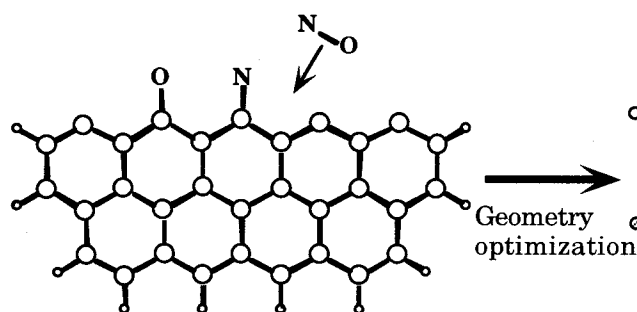


Figure 3. N_2 formation process in the reaction of the surface nitrogen complex with the NO molecule. The value of the atomic bond population for each bond is indicated.

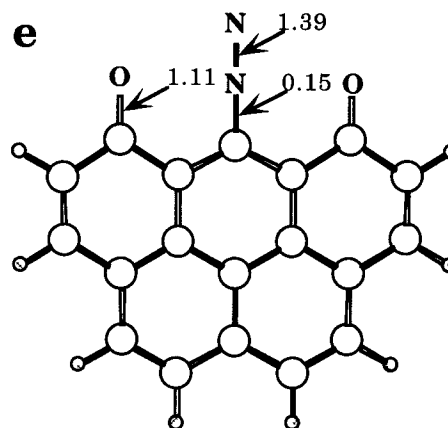


Figure 4. N_2 formation process from C(NN) species.

