Conversion of CO$_2$ into Formic Acid on Transition Metal-Porphyrin-like Graphene: First Principles Calculations

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ABSTRACT: Recently, transition metal (TM)-porphyrin-like graphene has been predicted to be a promising material for CO$_2$ capturing under favorable conditions. Such materials can capture CO$_2$ at 300 K and release it at 450 K. However, the captured CO$_2$ gas is mostly stored in oceans. With the aid of materials. Moreover, the selectivity of CO$_2$ from does not require CO$_2$ storage, it is expected to be an e...

1. INTRODUCTION

Carbon dioxide (CO$_2$), a greenhouse gas, is the main cause of global warming. The global surface temperature has increased significantly in recent years because of the drastic increase in CO$_2$ emissions, and the combustion of fossil fuels contributes significantly to this. As an essential step toward mitigating the climate change, considerable efforts have been made to develop technologies for collecting CO$_2$ from flue gases. The conventional methods for capturing CO$_2$ from flue gases rely heavily on the use of aqueous ammonia. However, this approach suffers from poor solvent regeneration and corrosion due to the toxic nature of the amine solution.

Recently, nanostructures or porous materials such as graphene, zeolites, and metal–organic frameworks have gained significant attention as CO$_2$ capturing materials because of the high regeneration of CO$_2$ gas through its physisorption on the material surface and the high capacity of the materials due to their large surface area (e.g., ~2600 m$^2$/g for graphene). However, their capture capacity significantly reduces under ambient conditions such as room temperature and atmospheric CO$_2$ pressure because of the low binding energy of CO$_2$ (approximately few tens of meV per CO$_2$ molecule) to these materials. Moreover, the selectivity of CO$_2$ from flue gases toward these materials is poor, and this largely hinders their use in CO$_2$ capture from flue gases.

More recently, through computational high-throughput screening based on first principles thermodynamics, metal-porphyrin-like graphene and Ca-decorated nanoribbons were shown to capture CO$_2$ from flue gases under ambient conditions. They could selectively capture CO$_2$ from other ambient gases such as H$_2$, N$_2$, and CH$_4$ with a CO$_2$ capture capacity of ~3 mmol/g. The Ca atoms and d orbitals of transition metals (TMs) have a predominant contribution to the binding of CO$_2$ during its capture. Meanwhile, transition metal-porphyrin-like graphene is synthesized in experiments. Therefore, metal-porphyrin-like graphene materials can serve as a promising reversible CO$_2$ capture material. However, storage of CO$_2$ in oceans and ground is still a matter of concern because of the high cost of CO$_2$ storage after its release on Sc- and Ti-porphyrin-like graphene.

Herein, we present a first principles study of a novel method for treating CO$_2$ following its capture. The proposed method converts CO$_2$ on metal-porphyrin-like graphene to formic acid (HCOOH) by adding H$_2$ as shown in Figure 1, which is slightly acidic and harmless; that is, it is environmentally friendly. CO$_2$ storage in oceans and ground can thus be avoided, resulting in easier management of the captured CO$_2$. Our results show that the addition of H$_2$ molecules to the CO$_2$ molecule adsorbed on the TM atom led to the formation of formic acid. The d orbitals of the TM atoms play a role in catalyzing the reaction between CO$_2$ and H$_2$ to form formic acid.
2. RESULTS AND DISCUSSION

To investigate the possibility of conversion of CO2 into formic acid on TM-porphyrin-like graphene, we performed the first principles calculations of CO2 adsorption on Sc- and Ti-porphyrin-like graphene. CO2 adsorption on TM results in the formation of the $\eta^2$ – CO2 structure through Dewar interaction.27 The TM-promoted reaction pathway of CO2 and H2 to form formic acid was obtained using the NEB method.38–42 The process by which the Sc and Ti atoms participate in this reaction can be divided into four stages involving four intermediate states. Each step was investigated with various trial coordinates. Here, we assume that the real process occurs in an energy surface, which corresponds to the minimum energy path for reaction. Thus, the minimum energy path of CO2 conversion that we presented in our paper is the most probable process in experiments.

When CO2 is adsorbed on the TM atom, it may adopt three configurations depending on the number of bonds. Based on hapticity, these three configurations can be classified as $\eta^1$, $\eta^2$, and $\eta^3$ as shown in Figure 2a–c. In the case of the Sc atom, CO2 has the strongest binding in the $\eta^2$ mode formed using two bonds, with a binding energy of 0.75 eV. Meanwhile, in the case of the Ti atom, the largest binding energy of 1.09 eV was observed in the $\eta^3$ mode. This suggests that CO2 binds to Sc- and Ti-porphyrin-like graphene by adopting the $\eta^1$ configuration.

We added H2 molecules to the CO2-adsorbed Sc-porphyrin-like graphene to obtain the optimized geometry upon adsorption. The distance between the Sc atom and H2 molecule was 3.41 Å, and the bond length was 0.75 Å. Moreover, formic acid could be generated from this configuration (Figure 1a). We performed the NEB calculations to investigate the energy barrier for the conversion of CO2 and H2 to formic acid on the Sc atom. Four transition states (TS1, TS2, TS3, and TS4) and five metastable states were found for this conversion (Figure 2d). The energy barriers corresponding to TS1, TS2, TS3, and TS4 were 13.5, 1.1, 10.5, and 9.0 kcal/mol, respectively. There were four intermediates (IM1, IM2, IM3, and IM4) corresponding to these transition states. For TS1, the H2 molecule is dissociated to HCOOH@Sc, in which the distance between the H atoms is 2.12 Å. Formic acid was generated with a net energy barrier of 33.7 kcal/mol, via the formation of four transition states and five intermediates (Figure 2d).

In Sc-porphyrin-like graphene, first, the H2 molecule dissociates into two hydrogen atoms that bind to a carbon atom and an extra oxygen atom that is not involved in TM binding. The bound CO2 combines with a H2 molecule to adopt the $\eta^1$ – CO2 configuration, eventually driving the binding reaction to generate formic acid via several stages. The NEB calculations confirmed that there were five steps in this reaction (Figure 2d). The H2 molecule adjacent to CO2 binds to the C and O atoms that do not participate in the $\eta^2$ bond formation. The energy barrier of this reaction is ~13.5 kcal/mol according to the NEB calculations. The step with the highest activation energy barrier according to the Arrhenius equation is the rate-determining step of the overall reaction; the other steps do not contribute to the overall rate of the reaction.

We next investigated the conversion of CO2 into formic acid on Ti-porphyrin-like graphene. CO2 was adsorbed on the Ti atom with a binding energy of 1.09 eV, and the distance
between CO₂ and the Ti atom was 2.06 Å. We performed NEB calculations to identify the TS and IM states between CO₂@Ti (initial state) and HCOOH + Ti (final state). Four TS and five IM states were also found between the initial and final states (Figure 3). The dissociation of CO₂ is similar to that on Sc-porphyrin-like graphene.

Now, we calculated the escape time from the initial state (IM0) to the first intermediate state (IM1) to investigate the practical conditions of the conversion because the step with the highest activation energy barrier is the rate-determining step of the overall reaction (Figure 4a), while the other steps do not contribute to the overall rate of the reaction. Using the first-order Polanyi–Wigner equation, 43 adsorption coverages (θ) between the two states in time t are expressed as

$$\frac{d\theta_i}{dt} = -k\theta_i$$  \hspace{1cm} (1)
$$\frac{d\theta_2}{dt} = k\theta_2$$  \hspace{1cm} (2)

where i and k indicate the index for representing the states (i = 1 for the initial state and i = 2 for the first intermediate state) and reaction rate constant, i.e., the frequency of collisions resulting in a reaction, respectively. The rate is expressed as follows by the Arrhenius equation

$$k = \nu e^{-E_i/k_BT}$$  \hspace{1cm} (3)

where \(\nu\), \(k_B\), and \(T\) denote the trial frequency, Boltzmann constant, and temperature, respectively.

$$\theta_i(t) = \theta_{i0} e^{-kt}$$  \hspace{1cm} (4)
$$\theta_2(t) = \theta_{20}(1 - e^{-kt})$$  \hspace{1cm} (5)

where \(\theta_{i0}\) indicates the initial value of the coverage at the initial state.

The calculated coverage for given temperatures is shown in Figure 4b, where the trial frequency is chosen to be 0.5 THz. The characteristic time for escape is from a few seconds to a few microseconds. From this result, we suggest that a suitable experiment condition for the conversion is \(\sim 300\) to 500 K.

To achieve the conversion of CO₂ to HCOOH, HCOOH attached to Sc or Ti should be released. Here, we carried out the evaluation of the desorption of HCOOH in equilibrium between the HCOOH molecule attached to Sc or Ti and HCOOH gas using the grand partition function. The fractional occupancy for the adsorption site, \(f(P, T)\), is expressed by the formula24

$$f(P, T) = \frac{e^{(\mu(P,T) - E_{ads})/k_BT}}{1 + e^{(\mu(P,T) - E_{ads})/k_BT}}$$  \hspace{1cm} (6)

where \(P\), \(\mu(P, T)\), and \(E_{ads}\) indicate the pressure of a gas, chemical potential of a gas at a given \(P\) and \(T\), and adsorption energy, respectively. The chemical potential of HCOOH gas was parameterized by the following formula

$$\mu_{ideal}(P, T) = \mu_{ideal}(P, T) + (A + B \times T)$$  \hspace{1cm} (7)

where \(\mu_{ideal}(P, T)\) denotes the chemical potential of the ideal gas model and constants \(A\) and \(B\) in a linearized excess part are 0.09350 eV and –1.09233 meV/K for HCOOH with \(R^2 = 0.999\) in the range from 1 atm to 1 atm and 200 to 700 K, respectively. A pressure-dependent term in an excess part is negligible in this range. HCOOH molecules are released on Sc- and Ti-porphyrin-like graphene at \(\sim 500\) K and \(\sim 10^{-6}\) bar as shown in Figure 5. In addition, we have already shown that the reaction for the conversion of CO₂ to HCOOH gas occurs at easily achievable conditions (Figure 4). Therefore, the activity for the conversion of CO₂ on Sc- and Ti-porphyrin-like graphene can be controlled by varying the temperature.

Figure 3. Calculated reaction energy of H₂ dissociation on CO₂ on Ti-porphyrin-like graphene to afford HCOOH obtained using the NEB method. Four transition states and five metastable states exist in the reaction pathway for the conversion of H₂ and CO₂ to HCOOH on Ti-porphyrin-like graphene.

Figure 4. (a) Schematic of the reaction energy of conversion of CO₂ on Sc-porphyrin-like graphene with H₂ to HCOOH, where the value of the activation barrier corresponds to 13.5 kcal/mol (TS1) between the initial state (IM0) and the first intermediate state (IM1) from the NEB calculations (Figure 3). (b) Calculated adsorption coverages as a function of time at 300, 400, and 500 K using eq 5.
We also studied the binding mechanism of formic acid on a TM-porphyrin-like graphene. It was found that the $\pi$ states of CO$_2$ and formic acid were significantly involved in hybridization with the $d$ states of Sc and Ti (Figure 6a–d). The charge density in the occupied states and charge density difference are shown in Figure 6e–h. This indicates that the presence of chemical bonding between the CO$_2$ molecule and Sc and Ti atoms can be explained using the Dewar–Chatt–Duncanson model, which describes TM–organic complexes in terms of electron donation (hybridization of empty TM $d$ states with filled $\pi$ states) and back donation (hybridization of filled TM $d$ states with empty $\pi$ states).27,28

We also performed the Bader charge analysis44–47 to better understand the charge transfer mechanism throughout the conversion. The positive value indicates that the charge is transferred from the surroundings to the atoms, while a negative value indicates the opposite phenomenon. In the case of Sc-porphyrin-like graphene, CO$_2$ adsorption results in a charge transfer of $-2.33$, $-3.44$, $1.97$, and $2.25$ electrons for the Sc, C, O$_1$, and O$_2$ atoms, respectively (Figure 7a), while the adsorption of HCOOH results in the charge transfer of $-2.34$, $-2.58$, $1.93$, $1.99$, $-0.13$, and $-1.00$ electrons for the Sc, C, O$_1$, O$_2$, H$_1$, and H$_2$ atoms, respectively (Figure 7b). In the case of Ti-porphyrin-like graphene, adsorption of CO$_2$ results in charge transfer of $-2.35$, $-2.32$, $1.53$, and $1.87$ electrons for the Ti, C, O$_1$, and O$_2$ atoms, respectively (Figure 7c), while the adsorption of HCOOH results in charge transfer of $-2.27$, $-2.45$, $1.93$, $1.95$, $-0.14$, and $-1.00$ electrons for the Ti, C, O$_1$, O$_2$, H$_1$, and H$_2$ atoms, respectively (Figure 7d). For both Sc- and Ti-porphyrin-like graphene, the Bader charge transfer analysis suggested that CO$_2$ was strongly chemisorbed. Further addition of H$_2$ resulted in the formation of formic acid, which was weakly adsorbed relative to CO$_2$, and therefore, the release of formic acid was practically feasible.

3. CONCLUSIONS

We investigated the feasibility of the TM-porphyrin-like graphene-mediated conversion of CO$_2$ to formic acid using first principles calculations. There were three significant findings in this study: (1) TM atoms aid the conversion of CO$_2$ into formic acid, (2) the $d$ orbitals play an important role in this conversion, and (3) there are three TS and four IM states in this reaction pathway. Our results show that TM-porphyrin-like graphene can be used for the conversion of CO$_2$ into formic acid upon addition of H$_2$. When exposed to H$_2$ gas, TM-porphyrin-like graphene can capture CO$_2$ and convert and release it in the form of formic acid. The Bader analysis reveals that CO$_2$ was strongly chemisorbed, and the addition of H$_2$
resulted in the formation of formic acid, which was relatively weakly adsorbed, thereby assisting the release of formic acid at a feasible temperature. Thus, we conclude that TM-porphyrin-like graphene can selectively capture CO$_2$ and transform it into formic acid, which is an environmentally friendly compound.

4. COMPUTATIONAL METHODS

We performed first principles density functional theory calculations using the Vienna Ab Initio Simulation Package (VASP) with the projector augmented wave (PAW) method for conversion of CO$_2$ on TM-porphyrin-like graphene adsorption, our model for the TM-porphyrin-like graphene comprised a 4 × 4 hexagonal supercell (Figure 8), and the composition of the supercell was C$_{2n}$N$_{4n}$TM$_1$, where C, N, and TM denote carbon, nitrogen, and transition metal atoms, respectively. The kinetic energy cutoff was set at 600 eV to ensure accurate calculations. The structure was geometrically optimized till the Hellmann–Feynman force acting on each atom was less than 0.01 eV/Å. We used 4 × 4 × 1 k-point sampling for each case, and the Brillouin zone integration was performed using the Monkhorst-Pack scheme. There is no dependence of the lattice constant as to the type of TM. Since the strength of the interaction between CO$_2$ and TM is ∼1 eV, which is much greater than that of a few meV, we did not consider the van der Waals interaction for the conversion process of CO$_2$. The nudged elastic band (NEB) calculations were performed to obtain the transient states between a particular configuration of CO$_2$ + H$_2$ and formic acid.

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Notes
The authors declare no competing financial interest.

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