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## Mechanistic study of NO oxidation on Cr–phthalocyanine: theoretical insight

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The reaction mechanisms of NO oxidation on chromium–phthalocyanine (CrPc) were elucidated using density functional theory calculations and compared with NO reduction. The results reveal that the reaction of NO oxidation on CrPc is a two-consecutive step pathway which produces NO<sub>2</sub> as a product. The first step can proceed through competitive Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms presenting the low activation barriers ( $E_a$ ) in a range of 0.1 to 0.5 eV with exothermic aspects. Moreover, the ER mechanism is found to be more feasible. In the second step, the reaction requires an  $E_a$  of 0.32 eV, which is considered as the rate determining step of the overall reaction. By comparing both NO oxidation and reduction, the results reveal that in the low O<sub>2</sub> system, CrPc converts NO to N<sub>2</sub> via a dimer (NO)<sub>2</sub> mechanism whereas in the excess O<sub>2</sub> system, it oxidizes NO to NO<sub>2</sub> easily. Both reaction systems required very low  $E_a$  values, thus this low cost CrPc catalyst could be a candidate for NO treatment at room temperature.

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### 1. Introduction

Nitrogen monoxide (NO) is one of the NO<sub>x</sub> compounds released from combustion engines. It can react with other reactants and form various toxic chemicals, photochemical smog and acid rain that have impact on human health and the environment.<sup>1</sup> From these reasons, NO removal technologies are necessary. Recent NO<sub>x</sub> removal techniques have been developed based on two major technologies called NO<sub>x</sub> storage/reduction (NSR) and selective catalytic reduction (SCR).<sup>2–4</sup> Catalytic based methods have been developed in order to improve the efficiency of NO<sub>x</sub> elimination with lower fuel consumption. Until now, NO reduction and oxidation using various catalysts have been explored by using experimental and computational tools.

According to their high reactivity and catalytic efficiency, metal and bimetal catalysts have been applied for various chemical reactions.<sup>5,6</sup> However, one of their limitations is the expensive price of metals. Therefore, other materials are used for supporting metal catalysts to reduce cost of them but yet to maintain their catalytic reactivity. For the NO<sub>x</sub> abatement technology, Pt–Ba/Al<sub>2</sub>O<sub>3</sub> has been broadly used in the NSR technique.<sup>3</sup> Vanadium-based catalysts have been widely used in

commercials for the ammonia selective catalytic reduction (NH<sub>3</sub>-SCR) of NO, however their drawback is the toxicity of vanadium.<sup>7</sup> To date, each of current materials and methods under investigation has its own advantages and disadvantages. Undoubtedly, improvement of high catalytic efficiency associated with a reasonable price is still a main challenge in the commercial NO<sub>x</sub> removal technology.

Regarding the discovery of the graphene sheet, other two dimensional (2D) materials have been received more attention and explored extensively these days. Metal-free and metal-supported 2D materials such as SiC,<sup>8</sup> silicene,<sup>9</sup> metal-graphene,<sup>10</sup> metal-graphene oxide (metal-GO)<sup>11</sup> and metal-boron nitride (metal-BN)<sup>12,13</sup> have been searched for using as adsorbates and catalysts in air treatment applications. Among those materials, 2D organometallic materials such as metal-phthalocyanines (MPcs) and metal-porphyrins (MPors), have been successfully synthesized by embedding metal species to the 2D-conjugated polymers.<sup>14–18</sup> These materials are controllable dispersed of central metal, which can prevent metal clustering. Additionally, their properties are tunable when replacing metals by other elements.<sup>19,20</sup> The embedded metal is highly stable preventing the aggregation into metal cluster which is one of the problems of using metal catalysts. Moreover, this structural diversity expands a wide range of usages. They have been proposed as catalysts in various reactions including the catalytic CO and NO<sub>x</sub> treatment technologies.<sup>21,22</sup> For instance, the decomposition of N<sub>2</sub>O over metal-porphyrins (metal: Ti, Cr, Fe, Co, Ni, Cu and Zn) were elucidated by using DFT calculations.<sup>22</sup> The result indicated that the TiPor is a promising catalyst for decomposing N<sub>2</sub>O into N<sub>2</sub> and O<sub>2</sub> products. Additionally, many

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Pc-based materials have been explored for NO<sub>x</sub> sensing by experimental and computational studies. For example, NiPc was investigated for NO<sup>23,24</sup> and FePc,<sup>25</sup> TiOPc, PbPc<sup>26,27</sup> and CuPc<sup>28–30</sup> were studied for detecting NO<sub>2</sub>.

In 2014, Li and Sun<sup>31</sup> simulated the CO and O<sub>2</sub> adsorption on transition metal embedded Pc sheets (MPc, M = Cr, Mn, Fe, Co, Ni). According to their adsorption results, MnPc, CrPc and FePc revealed the good adsorption ability toward the O<sub>2</sub> and CO molecules. They found that CrPc has the superior catalytic property for the CO oxidation. For the NO decomposition, the direct NO dissociation, which is breaking N–O bond and producing N and O atoms on surfaces, requires very high *E<sub>a</sub>* of 2.52 eV over CrPc<sup>32</sup> and more than 3.0 eV over Si-doped graphene.<sup>33</sup> Recently, we have proposed that CrPc is the potential catalyst for the NO reduction by forming (NO)<sub>2</sub> dimer.<sup>32</sup> Along with the exothermic aspect, the *E<sub>a</sub>* of the rate-determining step for the most favorable path of the NO reduction over CrPc is only 0.35 eV. This aspect implied that CrPc is feasible for reducing NO at low temperature.<sup>32</sup> However, this prediction was based on the absence of O<sub>2</sub> which is one of the main components in the gas mixture. In flue gas or exhaust gas mixture, O<sub>2</sub> is believed to be involved in the reaction of NO decomposition. Thus, we expanded our study by considering the involvement of O<sub>2</sub> in the reaction.

In this study, we proposed that NO is oxidized by O<sub>2</sub> on the CrPc catalyst. Two major mechanisms called Eley–Rideal (ER) and Langmuir–Hinshelwood (LH) mechanisms were theoretically investigated. The rate-determining steps were intensively determined from the activation energy (*E<sub>a</sub>*) calculations. The obtained results from this NO oxidation is compared and discussed with the NO reduction reported in our previous work.<sup>32</sup> The catalytic reactivity of other materials for similar reactions were also discussed.

## 2. Method

All calculations were carried out in a framework of the spin polarization DFT method using a generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional.<sup>34</sup> A double numerical plus polarization (DNP) basis set<sup>35</sup> was used with the real space global orbital cutoff radius as 4.8 Å. A smearing of electronic occupations was set as 5.0 × 10<sup>−3</sup> Ha. An energy threshold was 1.0 × 10<sup>−5</sup> Ha, while a force threshold was 2.0 × 10<sup>−3</sup> Ha Å<sup>−1</sup>. Self-consistent field (SCF) calculations were carried out with a convergence criterion of 1.0 × 10<sup>−5</sup> Ha. All electron calculations were performed for the C, N, O, and H atoms, and a relativistic effect included effective potential was used to represent core electrons of the Cr atom. All atoms in the system were allowed to relax during the geometry optimizations. The *z*-direction was set as the perpendicular to the plane of the CrPc monolayer while the *x*- and *y*-directions were in parallel, see Fig. 1. The supercell length in the *z*-direction was set to 15 Å to avoid the artificial interaction of periodic images. The Brillouin zone sampling was 5 × 5 × 1 *k*-points. A method for transition state (TS) search was employed by a linear synchronous transit (LST) method, followed by repeated conjugated gradient (CG) refinements, and then quadratic

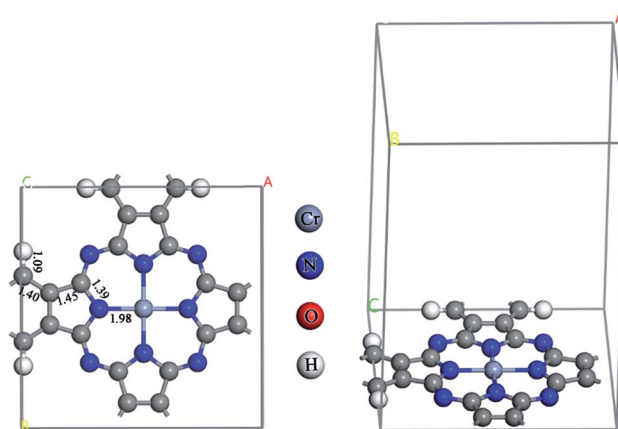


Fig. 1 Top view (left) and side view (right) of the unit cell of CrPc monolayer.

synchronous transit (QST) maximizations<sup>36</sup> and repeated CG refinements until the TS is located. Finally, a nudged elastic band (NEB) method<sup>37</sup> was performed to obtain a minimum energy pathway (MEP). The vibrational frequency calculation was performed on the obtained TS structure to ensure that it has only one imaginary frequency corresponding to the reaction coordinate. The Hirshfeld charge was used to explain charge on atoms and charge density difference between the adsorbate and CrPc in the adsorption complexes. All calculations were performed on the Dmol<sup>3</sup> module<sup>35,38</sup> implemented in Material Studio 8.0.

Based on our previous report,<sup>32</sup> the stable sites of NO, O<sub>2</sub> as well as the related reactive species were stable on the Cr metal site of the CrPc surface. In this work, we reconsidered all possible configurations of each gas molecules on CrPc and the most preferable site and configuration of each gas adsorption are presented. The adsorption energies (*E<sub>ad</sub>*) of NO, O<sub>2</sub>, and N<sub>2</sub>O on the CrPc catalyst can be calculated by the following equation:

$$E_{ad} = E_{gas/CrPc} - E_{CrPc} - E_{gas}$$

where *E<sub>gas/CrPc</sub>*, *E<sub>CrPc</sub>*, *E<sub>gas</sub>* represent total energies of the gas/CrPc adsorption complex, the CrPc catalyst and the isolated gas molecule, respectively. More negative *E<sub>ad</sub>* value implies more energetic stability when the gas is adsorbed on the surface compared to its isolated constituent.

## 3. Results

The optimized CrPc monolayer with the bond lengths is illustrated in Fig. 1. The bond lengths between the central Cr atom and each neighboring N atom are equivalent at 1.98 Å, which is similar to the value of 2.001 Å calculated by using GGA + U method (the *U* parameter is entered to GGA calculation to treat the strong on-site Coulomb interaction of localized d-electrons of Cr).<sup>39</sup> The reaction of NO oxidation to produce NO<sub>2</sub> can be explained by 2NO + O<sub>2</sub> → 2NO<sub>2</sub>. In the first part, the adsorption of O<sub>2</sub>, NO and NO<sub>2</sub> on CrPc are discussed in order to understand the interactions between the reactant or product compounds



and the catalyst. In the second part, PES diagrams of the possible mechanisms are compared to find the most favorable pathway.

### 3.1 Gas adsorption on CrPc

Based on types of gases involved in the NO oxidation, adsorbed gases over the CrPc sheets, which are O<sub>2</sub>/CrPc, NO/CrPc and NO<sub>2</sub>/CrPc were calculated. In the previous study,<sup>32</sup> we had carefully studied the possible adsorption configurations of NO on CrPc. It was found that a NO prefers the N-bound adsorption mode in which the terminal N atom of NO has a strong bond with the Cr site. To compare with other gas species, the

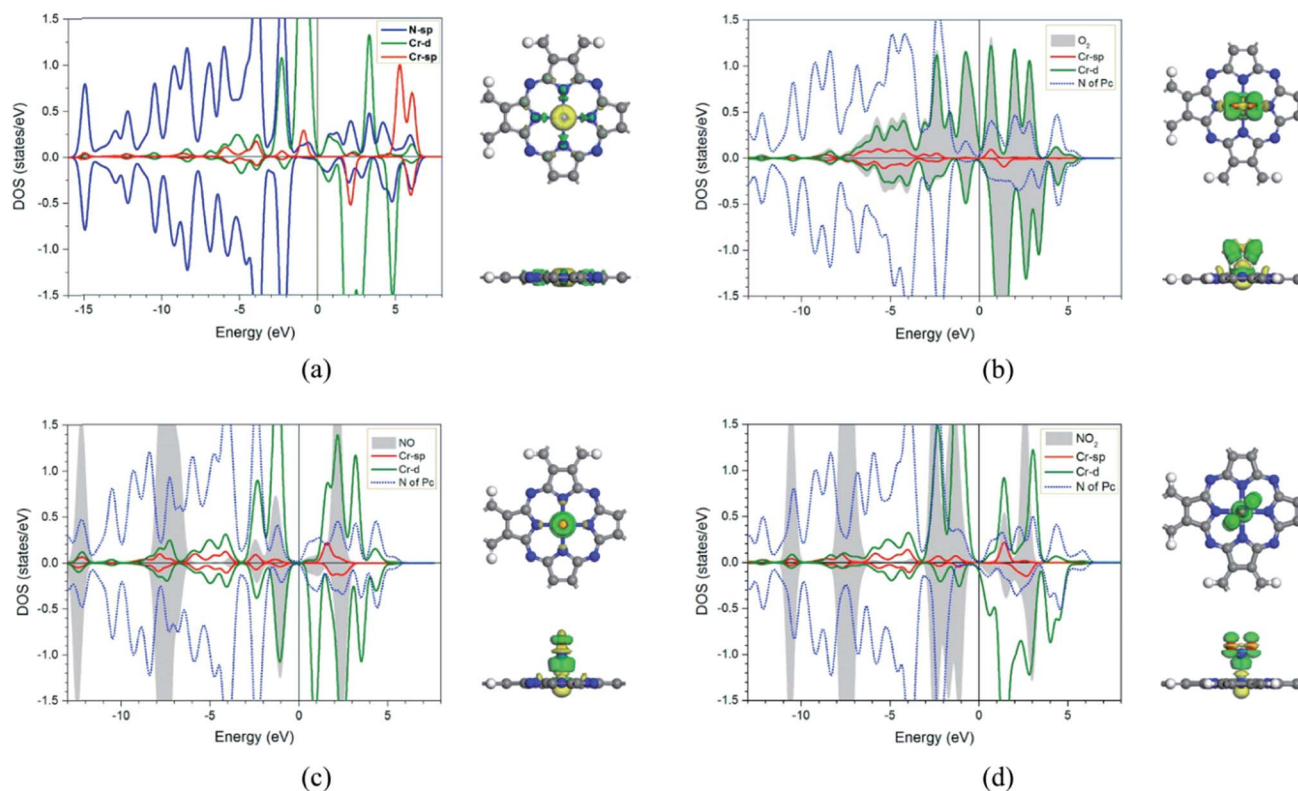
**Table 1** The calculated  $E_{\text{ad}}$  values (in eV) of gas adsorption on CrPc and their corresponding structural parameters (in Å). The values in the parentheses are the bond lengths of isolated gases

Adsorption complex	$E_{\text{ad}}$ (eV)	Structural parameter	
		Bond	Length (Å)
O <sub>2</sub> /CrPc	−1.13	Cr–O	1.85
		O–O	1.40 (1.23)
NO/CrPc <sup>32</sup>	−2.07	Cr–N	1.67
		NO	1.18 (1.16)
NO <sub>2</sub> /CrPc	−1.28	Cr–N	2.00
		NO	1.23 (1.21)

calculated  $E_{\text{ad}}$  values, charges and corresponding structural parameters are summarized in Table 1. The bond lengths of isolated gases are given in the parentheses. From the calculated  $E_{\text{ad}}$ , the order of adsorption strength is NO/CrPc (−2.07 eV) > NO<sub>2</sub>/CrPc (−1.28 eV) > O<sub>2</sub>/CrPc (−1.13 eV). All studied gases have the strong chemical bonds with the CrPc substrate. Additionally, the NO reveals the stronger binding strength with CrPc compared with NO/MnPc ( $E_{\text{ad}}$  = −1.73 eV), NO/CoPc ( $E_{\text{ad}}$  = −1.55 eV) and NO/FePc ( $E_{\text{ad}}$  = −1.90 eV) systems reported in literature.<sup>21</sup>

The O<sub>2</sub>/CrPc presents the parallel adsorption configuration with the  $E_{\text{ad}}$  of −1.13 eV. The oxygen molecule is activated and the O–O bond is elongated to be 1.40 Å compared with that of the isolated O<sub>2</sub> molecule (1.23 Å), which is in good agreement with other studies.<sup>31</sup> For the NO<sub>2</sub>/CrPc, NO<sub>2</sub> attaches to the central Cr atom with the distance of 2.00 Å and the  $E_{\text{ad}}$  of −1.28 eV. This interaction is much stronger than NO<sub>2</sub>/CuPc which has the  $E_{\text{ad}}$  of −0.40 eV.<sup>40</sup> Comparing with isolated gases, the adsorbed O–O bond is increased about 0.17 Å, while bonds of adsorbed NO and NO<sub>2</sub> are less lengthened in range of 0.02–0.03 Å.

In addition, the electronic charge properties of the pre-adsorbed and gas-adsorbed CrPc are clarified to give a deeper understanding. The density of state (DOS) and electron density difference of the bare CrPc, O<sub>2</sub>/CrPc, NO/CrPc and NO<sub>2</sub>/CrPc systems are illustrated in Fig. 2a–d, respectively. For the DOS



**Fig. 2** DOS (left panel) and electron density difference in top- and side-views (right panel) of (a) CrPc (b) O<sub>2</sub> adsorbed CrPc, (c) NO adsorbed CrPc and (d) NO<sub>2</sub> adsorbed CrPc. The green and yellow regions represent electron density accumulation and depletion regions, respectively. The isosurface value is  $\pm 0.02$ .



analysis (in the left panel), the blue, green and red peaks present the partial DOS of N-sp, Cr-d and Cr-sp orbitals of CrPc, correspondingly. In gas-adsorbed systems, the grey peaks depict the partial DOS of the adsorbed gases. The Fermi level ( $E_f$ ) is set to zero eV. For the charge difference analysis (in the right panel), the green and yellow isosurfaces signify the electron density accumulation and depletion, respectively. In each system, the charge difference analysis is illustrated in both top- and side-views.

In Fig. 2a, the partial DOS of the bare CrPc are projected. The interaction between the central Cr atom and its neighboring N atoms is indicated by the overlapped peaks of the DOS plot in the right panel. For the partial DOS of Cr, the asymmetric peaks of the spin-up and spin-down components indicate the magnetic characteristic of the metal site. The charge difference explains that the electrons are reduced at the Cr site while they are accumulated between Cr and N atoms. This feature also relates to the partial charge values, which are +0.96 e of Cr atom and -0.62 e of the neighboring N atom, reported in the previous study.<sup>22</sup>

For the activated O<sub>2</sub> on CrPc, the side-on interaction of O<sub>2</sub> on CrPc is dominated by the overlapping of the LUMO ( $2\pi^*$ ) of O<sub>2</sub> and the highest occupied molecular orbital (HOMO-3) of CrPc.<sup>31</sup> This hybridization feature can be observed from the overlapping of those grey peaks of O orbitals and green peaks of Cr-d orbitals as shown in the left panel of Fig. 2b. The charge difference of O<sub>2</sub>/CrPc is displayed in the right panel. At the Cr site, the electron density on one side of the CrPc sheet is reduced while the accumulation can be observed on another side. This characteristic indicates the bonding between Cr and O atoms. The accumulated electron regions are presented by the green basin around oxygens.

The interaction between NO and CrPc can be described by the symmetrically interaction between the lowest unoccupied molecular orbitals (LUMO) of CrPc on the  $d\pi$  and the  $2\pi^*$  orbitals of NO.<sup>32</sup> The HOMO-LUMO gap is wider as compared to that of the bare CrPc sheet. A strong hybridization in both spin-up and spin-down states of the Cr-d and NO orbitals is clearly demonstrated in Fig. 2c. Especially, in the spin-down states the  $2\pi^*$  orbital of NO molecule is dominantly occupied. Considering the interaction between CrPc and NO, the electron accumulation, which is the green region of the charge difference analysis, exists between the Cr and N atoms. On the other hand, the electron density at the N-O bond is decreased. Likewise, the interaction between NO<sub>2</sub> and CrPc can be observed from the DOS and charge difference analyses as illustrated in Fig. 2d. The hybridization between the valence states of NO<sub>2</sub> and Cr is dominated for their bonding. Similar to other cases, the accumulation of electron density between the Cr and the adsorbate molecule can be observed from the charge differences.

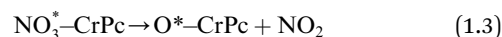
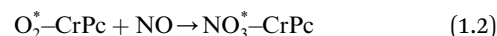
### 3.2 Mechanisms of NO oxidation on CrPc

Due to the much stronger adsorption energy of NO than O<sub>2</sub>, NO will be fully occupied on the Cr site if concentrations of O<sub>2</sub>, NO and Cr active site in the system are equivalent. It is simply predicted that the NO reduction would proceed in this case.<sup>32</sup>

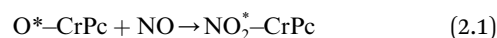
On the other hand, if O<sub>2</sub> is abundant in the system, O<sub>2</sub> and NO could be competitively occupied on the Cr active site; the NO oxidation by O<sub>2</sub> will further proceed. The detailed mechanisms of NO oxidation on CrPc are given in this section.

The overall reaction of NO oxidation is  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ . The proposed mechanisms of NO oxidation on CrPc are composed of following individual steps:

Step 1: the first NO oxidation to produce the first NO<sub>2</sub> by



Step 2: the second NO oxidation to produce the second NO<sub>2</sub> by



**3.2.1 The first NO oxidation:  $\text{NO} + \text{O}_2^* \rightarrow \text{NO}_2 + \text{O}^*$ .** In this work, two possible mechanisms called ER and LH mechanisms are elucidated for the first NO oxidation step. The ER pathway can be described by eqn (1.1) to (1.3). The LH mechanism is explained by eqn (1.4) to (1.5).

**3.2.1.1 ER mechanism.** In the O<sub>2</sub> abundant system, O<sub>2</sub> molecule is adsorbed and activated on the catalyst first. This elementary step can be described by eqn (1.1). As presented in the previous section, the O<sub>2</sub> molecule is simultaneously adsorbed on the CrPc catalyst with the  $E_{\text{ad}}$  of -1.13 eV. Next, NO interacts with the pre-adsorbed O<sub>2</sub>\* to form the first NO<sub>2</sub> molecule. The structures and corresponding energy profile of the ER mechanism are depicted in Fig. 3 and 4, respectively. The NO molecule interacts with the activated O<sub>2</sub>\* (IS1) by inserting between two O atoms and forms the NO<sub>3</sub>\* intermediate (INT1) on the Cr atom. When IS1 transforms to INT1, the N initiates bonds with O atoms while the O-O and O-Cr bonds are lengthened from 1.40 to 2.12 Å and 1.85 to 2.00 Å, respectively. This path is the exothermic process which is required the small  $E_a$  of 0.19 eV. The transition state (TS1) is confirmed by a single negative vibrational frequency of 167.27i cm<sup>-1</sup>. Next, the successive step proceeds through the INT1, transition state (TS2), and final state (FS1). The TS2 and the FS1 are illustrated in Fig. 3. The  $E_a$  value is only 0.06 eV, which is less than the previous step. At the TS2 state, elongation of one Cr-O bond (2.43 Å) and O-N bond (1.34 Å) are observed. This transition state is confirmed by the frequency of 158.15i cm<sup>-1</sup>. At the final state, those bonds are completely dissociated to release the first NO<sub>2</sub> molecule. One oxygen atom remains on CrPc and it will interact with the second NO molecule in the further step. According to the relative energy, FS1 is very thermodynamically stable than IS1. It is noted



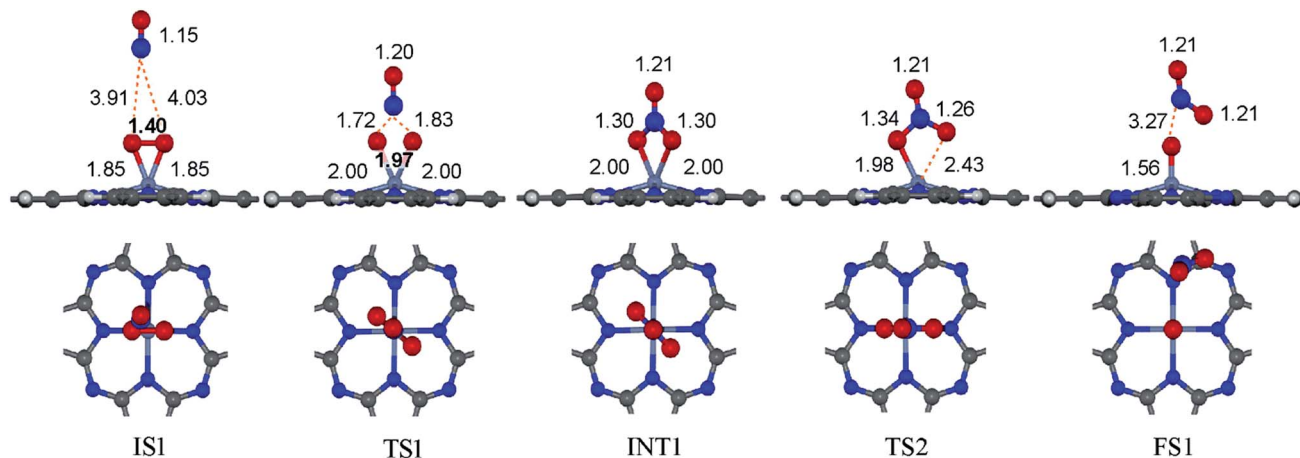


Fig. 3 Top and side views of initial, intermediate and final structures of the ER mechanism.

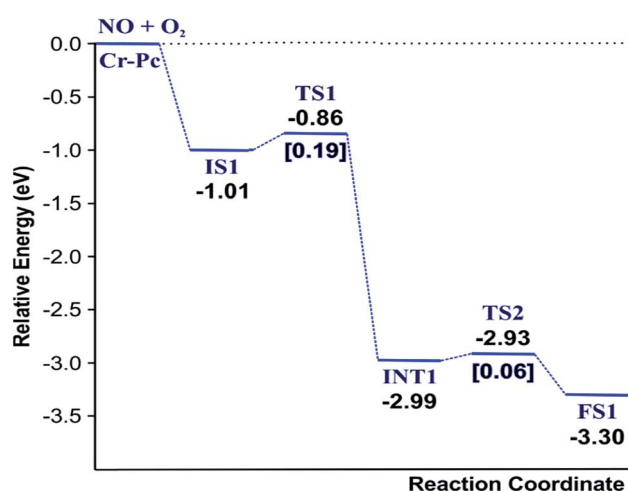


Fig. 4 Reaction pathway of the ER mechanism for the first  $\text{NO}_2$  production.

that the product state of each elementary step has lower relative energy than its preceding state. The reaction proceeds through the very small  $E_a$  values and large exothermic reaction. This feature indicates that this ER mechanism is kinetically and thermodynamically favorable reaction.

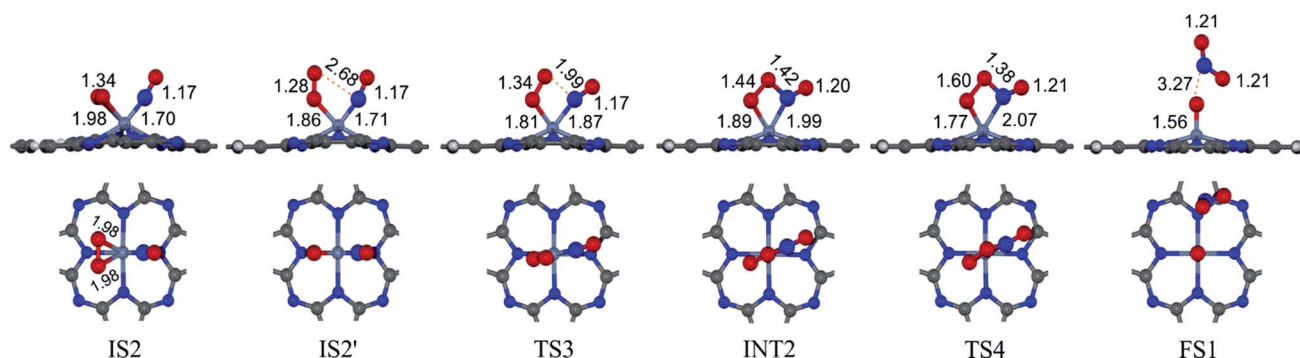


Fig. 5 Top and side views of initial, intermediate and final structures of the LH mechanism.

**3.2.1.2 LH mechanism.** The structures and energy profile of the LH mechanism are expressed in Fig. 5 and 6, respectively. In LH mechanism,  $\text{O}_2$  and  $\text{NO}$  are initially co-adsorbed on  $\text{CrPc}$  as shown in Fig. 5. At the initial step, there are two co-adsorbed configurations which are  $\text{IS2}$  and  $\text{IS2}'$  (see Fig. 5). Both  $\text{O}$  atoms bind with the  $\text{Cr}$  atom in the  $\text{IS2}$  form, while only one  $\text{O}$  atom is attached with the  $\text{Cr}$  atom in  $\text{IS2}'$  form. The energy difference of 0.43 eV is for transforming  $\text{IS2}$  to  $\text{IS2}'$ . Then,  $\text{IS2}'$  forms the peroxide-like  $\text{O-N-O-O}$  intermediate ( $\text{INT2}$ ) via the transition state ( $\text{TS3}$ ). This path is the endothermic process requiring the  $E_a$  value of 0.50 eV. In the following step,  $\text{NO}_2$  is released and one  $\text{O}$  atom remains on the catalyst. This step occurs through  $\text{INT2}$ ,  $\text{TS4}$  and  $\text{FS1}$ , sequentially. The  $\text{O-O}$  bond starts rupturing by lengthening bond from 1.44 Å in  $\text{INT2}$  to be 1.60 Å in  $\text{TS4}$ . The small  $E_a$  of 0.10 eV is required to overcome this barrier. This is the exothermic process. The vibrational frequencies of  $\text{TS3}$  and  $\text{TS4}$  are  $-302.23i$  and  $-621.07i$   $\text{cm}^{-1}$ , respectively. Finally, the first  $\text{NO}_2$  product is released and one  $\text{O}$  atom remains on the catalyst.

As a result, low energy barriers can be observed in both mechanisms. The  $E_a$  energies are required in range of 0.1 to 0.2 eV and 0.1 to 0.5 for the ER and LH mechanisms, respectively. However, the ER pathway is the preference path due to its



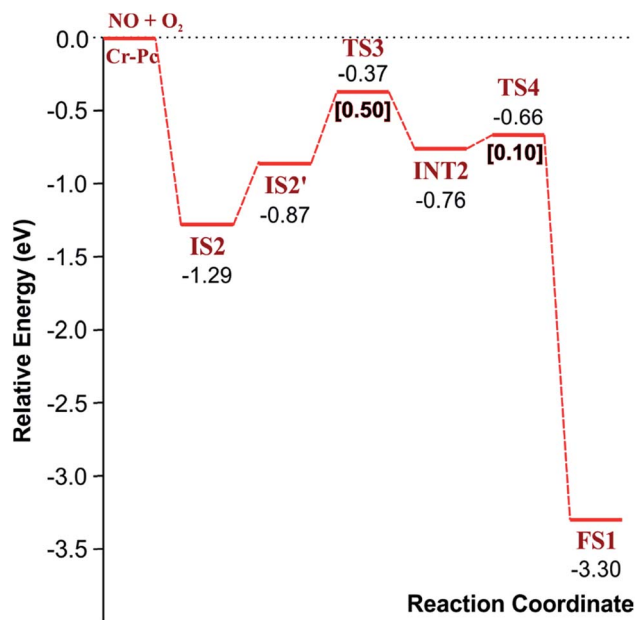


Fig. 6 Reaction pathway of the LH mechanism for the first  $\text{NO}_2$  production.

lower  $E_a$  of the rate limiting step and its lower relative energies of intermediate states compared to those of the LH pathway.

**3.2.2 The second NO oxidation:  $\text{NO} + \text{O}^* \rightarrow \text{NO}_2$ .** After step 1 of those LH and ER paths, the first  $\text{NO}_2$  is released and one O atom is bound to the CrPc sheet. Another NO molecule reacts to the remaining  $\text{O}^*$  on CrPc to produce the second  $\text{NO}_2$  product and the catalyst is recovered. The structures and corresponding energy profile of this mechanism are given in Fig. 7 and 8, respectively. The reaction starts from the IS3 state that NO molecule interacts with  $\text{O}^*$  on CrPc. At the TS5 state, NO initiates a bond with the O atom with the length of 1.94 Å for forming  $\text{NO}_2$  at the consecutive state (FS2). This transition state is confirmed by the frequency of  $114.70\text{ i cm}^{-1}$ . This second  $\text{NO}_2$  production requires a low  $E_a$  of 0.33 eV. This second NO oxidation step expresses slightly endothermic aspect where the

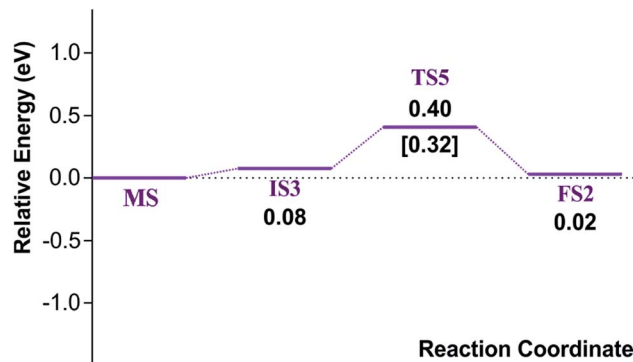


Fig. 8 The reaction pathway of the second NO oxidation.

relative energy of FS2 is slightly lower than the previous step  $\sim 0.06$  eV. Eventually,  $\text{NO}_2$  is completely desorbed from the CrPc surface at the final step by requiring energy of 1.28 eV.

Finally, the energy profiles of all steps are compared in Fig. 9. In summary, the first NO oxidation step requires low energy to proceed. This step prefers the ER mechanism with the  $E_a$  of 0.19 eV for the rate-determining step and the exothermic aspect. Although, the LH mechanism has higher  $E_a$  values than the ER mechanism, it still has the moderate  $E_a$  with the exothermicity. For forming the second  $\text{NO}_2$ , the  $E_a$  is slightly higher than the first  $\text{NO}_2$  formation with slightly exothermic feature. The oxidation can occur easily due to low activation energy pathway. Our result suggested that the overall reaction pathways of NO oxidation on CrPc are thermodynamically and kinetically favorable. Thus, this CrPc monolayer is one of potential catalysts for the NO oxidation at low temperature.

Considering the calculated  $E_a$  values of NO removal processes catalyzed by CrPc catalyst in Table 2, the NO oxidation by  $\text{O}_2$  studied in this work tends to occur slightly easier than the NO reduction by NO from our previous work.<sup>32</sup> The calculated  $E_a$  values of the rate determining steps are 0.32 eV for the oxidation and 0.35 eV for the reduction, respectively. These small  $E_a$  values indicate the high activity of CrPc for both reactions at room temperature or even lower. Moreover, the rate-limiting

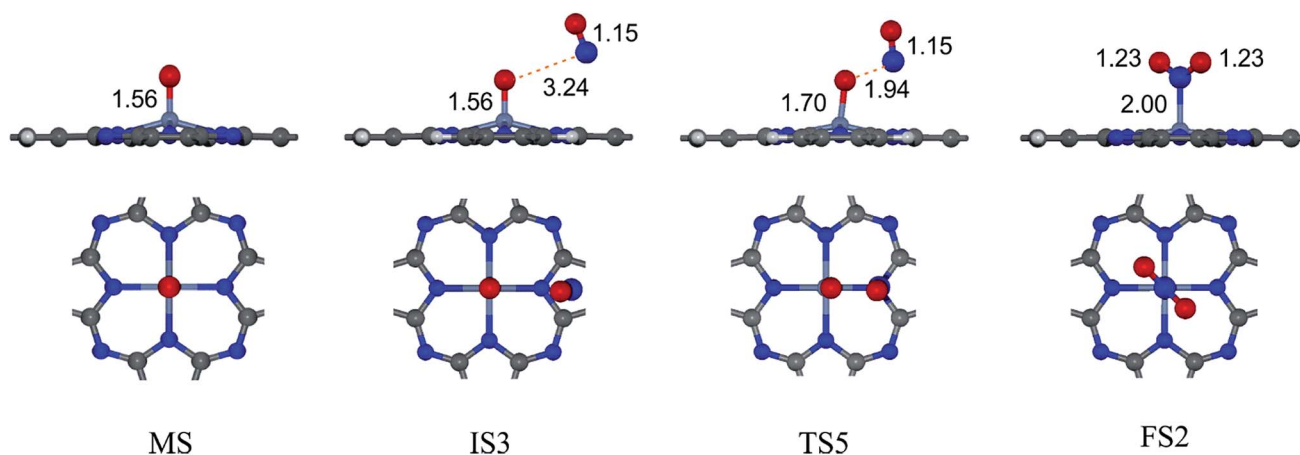


Fig. 7 Top and side views of initial, intermediate and final structures of the second NO oxidation.



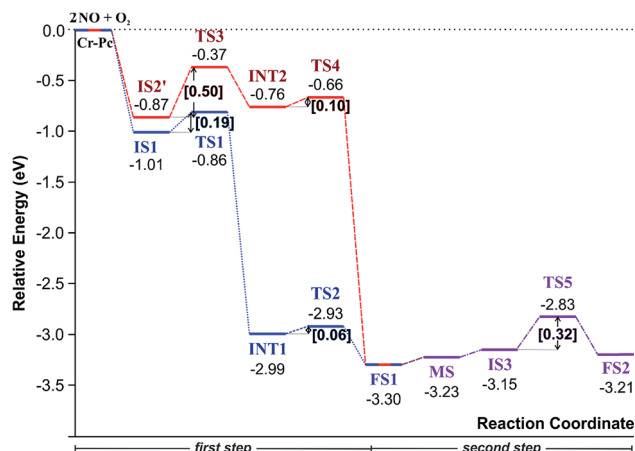


Fig. 9 A PES diagram of all proposed pathways.

Table 2 Comparison of the rate-limiting steps and the corresponding activation energy barriers ( $E_a$ ) for the NO and CO decomposition reactions on the 2D catalysts in literature

Catalyst	Reaction steps	$E_a$ (eV)
CrPc (this work)	$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}^*$	0.19
	$\text{NO} + \text{O}^* \rightarrow \text{NO}_2^*$	0.32
CrPc <sup>32</sup>	$\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}^*$	0.35
CrPc <sup>31</sup>	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$	0.55
	$\text{CO} + \text{O}^* \rightarrow \text{CO}_2$	0.46
Pt/TiPc <sup>41</sup>	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$	0.55
Si/graphene <sup>42</sup>	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$	0.43
	$\text{CO} + \text{O}^* \rightarrow \text{CO}_2$	0.07
SiC <sup>43</sup>	$\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}$	0.72
Silicene <sup>44</sup>	$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^*$	0.45
Si/graphene <sup>33</sup>	$\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}^*$	0.46
Pt/graphene <sup>10</sup>	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$	0.15, 0.35
	$\text{CO} + \text{O}^* \rightarrow \text{CO}_2$	0.46
N/Graphene (NG) <sup>45</sup>	$(\text{NO})_2 \rightarrow \text{N}_2\text{O} + \text{O}^*$	0.70
	$\text{N}_2\text{O} + \text{O} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2$	0.27
	$\text{N}_2\text{O} + \text{N}_2 \rightarrow \text{N}_2 + \text{O}^*$	0.05
Pt/oxidized graphene <sup>46</sup>	$\text{NO} + \text{O}^* \rightarrow \text{NO}_2$	0.16
	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$	0.76
	$\text{CO} + \text{O}^* \rightarrow \text{CO}_2$	0.04

steps and the corresponding reaction barriers for the NO and CO decomposition reactions on the selected 2D-based catalysts from literatures are summarized in Table 2. Comparing with CO oxidation on CrPc reported in literature,<sup>31</sup> the NO oxidation occurs easier than the CO oxidation. Considering other 2D-materials, their catalytic reactivities presented by the calculated  $E_a$  values tend to lower than that of CrPc for the NO oxidation and reduction. Among the 2D-materials reported in literature the CrPc material is, therefore, a candidate catalysts for low-temperature  $\text{NO}_x$  removal.

## 4. Conclusion

The detailed mechanisms of NO oxidation on the CrPc sheet were studied by performing the DFT calculations with PBE functional. There are two oxidation steps proposed in this

study. The first NO oxidation begins with the reaction between NO and  $\text{O}_2$  over CrPc to produce  $\text{NO}_2$  molecule and one O atom attached on Cr. In this step, the simulated ER and LH mechanisms present the competitive nature with comparable  $E_a$  and the exothermic aspect. As a result, the ER pathway, which is more favorable pathway, has lower  $E_a$  than LH pathway about 0.3 eV. Based on these energetic aspects, the ER mechanism is the kinetically and thermodynamically preference pathway for the first  $\text{NO}_2$  production. The second NO oxidation step (*i.e.*  $\text{NO} + \text{O}^* \rightarrow \text{NO}_2$ ) reveals the  $E_a$  of 0.32 eV which is considered as the rate determining step of the overall reaction. Comparison of the NO oxidation in this work with the NO reduction in our previous report,<sup>30</sup> the NO adsorption is two-fold stronger than the  $\text{O}_2$  indicating the NO molecule would be easily occupied on the Cr active site to follow the NO reduction. Under the  $\text{O}_2$  abundant condition, the NO oxidation by  $\text{O}_2$  would be competitive. However, both reactions proceed with low  $E_a$  (<0.35 eV) and high exothermicity, indicating that CrPc is the active catalyst for NO removal at room temperature or even lower.

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