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First-Principles Investigations of Single Metal Atoms (Sc, Ti, V, Cr, Mn, and Ni) Embedded in Hexagonal Boron Nitride Nanosheets for the Catalysis of CO Oxidation

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Abstract: We evaluated isolated transition metal atoms (Sc, Ti, V, Cr, Mn, and Ni) embedded in hexagonal-BN as novel single atom catalysts for CO oxidation. We predicted that embedded Ni atoms should have superior performance for this task. Ti, V, and Mn bind CO₂ too strongly and so the reaction will not proceed smoothly. We studied the detailed reaction processes for Sc, Cr, and Ni. The Langmuir–Hinshelwood (LH), Eley–Rideal (ER), and the new termolecular Eley–Rideal (TER) processes for CO oxidation were investigated. Sc was not effective. Cr primarily used the ER process, although the barrier was relatively large at 1.30 eV. Ni was the best of the group, with a 0.44 eV barrier for LH, and a 0.47 eV barrier for TER. Therefore, we predicted that the LH and TER processes could operate at relatively low temperatures between 300 and 500 K.

Keywords: hexagonal boron nitride; single atom catalyst; CO oxidation; catalysis

1. Introduction

Catalytic converters play a crucial role in the reduction of toxic emissions from automobiles via the oxidation reaction of carbon monoxide (CO) [1]. This reaction has also become a prototype for the examination of the activity, selectivity, and durability of heterogeneous catalysts [2]. In recent decades, several groups have investigated and studied catalysts for CO oxidation. Noble metals including Pt [3–5], Rh [6,7], Pd [7,8], and Au [9–11] have been evaluated for the catalysis of CO oxidation. Noble metals are expensive and depletable resources. Therefore, it is important to find less expensive and more abundant alternatives. Over time, catalyst particle sizes have been substantially reduced. Potentially, one could reduce the size of the catalyst particles all the way to single atoms. Remarkably, these single atom metal catalysts show great potential to enhance catalytic activity and selectivity. [12,13].

There has been remarkable progress in experimental synthesis and the evaluation of single atom catalysts (SAC) [13–15]. Common synthetic methods include atomic layer deposition, wet chemistry, and soft-landing techniques. Preventing the aggregation of individual atoms into clusters is an important issue that has to be solved for each material. In 2011, Qiao et al. [13] were the first to

prepare a practical Pt SAC supported by an iron oxide substrate (Pt₁/FeOx). This had excellent catalytic performance, and it demonstrated that single atom catalysts could work experimentally. More recently, two-dimensional materials such as freestanding hexagonal boron nitride monolayers (h-BN) [16,17], graphene [18–20], graphyne [21,22], and MoS₂ [23] have been proposed as substrates for single atom catalysts. These materials are predicted to have high catalytic activity for CO oxidation. These materials have high surface area and high thermal stability. Some experimental examples exist, such as individual Fe atoms mounted on graphene for the oxidation of benzene (which operates at 300 K) [24], and individual Co atoms mounted on nitrogen doped graphene (to produce hydrogen) [25]. Our group proposed Mn embedded in graphene as a potential new SAC based on DFT calculations [26].

One can produce defects in h-BN nanosheets or nanotubes using controlled electron beam irradiation [27,28]. These defects consist of either boron or nitrogen vacancies (in this paper, we will focus on the B vacancy as described below). h-BN is normally a very inert and non-reactive material. The production of vacancies produces binding sites, which can capture individual metal atoms. These metal atoms can be strongly bound to the substrate, and they may also act as active catalysts under the right conditions. These metal-doped SACs may exhibit unique catalytic properties due to their unusual geometry and unsaturated metal sites. Recently, there have been numerous computational studies to design and evaluate h-BN SACs for the catalysis of CO oxidation [16,17,29–32]. For this purpose, Lin et al. have evaluated Cu, Ag, Au, Pt, Rh, Pd, Fe, Co, and Ir h-BN SACs [16]. They found that Co should be a good SAC for CO oxidation. Liu et al. studied Cu h-BN SACs [17]. Liu et al., Mao et al., Zhao et al., and Lu et al. studied Pt, Au, Fe, and Co h-BN SACs using DFT, respectively [29–32]. Lu et al. studied Ag h-BN in 2017 [33]. Sc, Ti, V, Cr, Mn, and Ni embedded in h-BN for CO oxidation have yet to be studied.

In this paper, we evaluated isolated Sc, Ti, V, Cr, Mn, and Ni atoms located at defect sites in h-BN for use as single atom catalysts using density functional theory. We investigated the stability of these structures, and the catalytic activity for CO oxidation. We observed that Ni-h-BN is a promising SAC candidate.

2. Results and Discussion

2.1. Geometry and Stability

For the h-BN monolayer, there are two types of monovacancies: The B-vacancy and the N-vacancy [27,34]. These involve the removal of a single B or N atom from the h-BN. We focused on the M-BN materials with individual Sc, Ti, V, Cr, Mn, or Ni metal atoms embedded into a vacancy. For metal atom catalytic sites located at the B-vacancy, (BM-BN), they were located at the center of the defect. The longest Sc–N bond was 1.96 Å whilst the shortest Ni–N bond was 1.80 Å. Given the bond length, the Sc atoms were slightly up out of the h-BN plane. To evaluate the stability of these M-BN materials, the binding energies of the metal atoms at the B-vacancy and at the N-vacancy were calculated. For BM-BN, the binding energies were very strong and ranged from 8.4 to 12 eV (see Figure 1). For the N-vacancy (NM-BN) materials, the binding energies were much weaker and ranged from 3.0 to 5.8 eV. This was consistent with previous experimental and theoretical work [27]. Owing to the high binding energy, for the rest of the paper, we investigated the B-vacancy BM-BN materials.

To evaluate the mobility of TM atoms on BM-BN, we calculated the diffusion barriers for the Ni atom as a representative example. We considered the atom moving from a defect site to a hollow site. Figure 2a shows the structures of the initial state (IS), transition state (TS), and final state (FS) for this process. Fermi level (E_F) was set to zero.

We found a barrier of 5.5 eV from IS to hollow site 1, and 6.3 eV from IS to hollow site 2. These barriers were larger than the 3.8 and 5.3 eV barriers for the Pd-BN sheet [35]. Our results showed that, under normal conditions, Ni atoms would not diffuse significantly away from the B-vacancy sites, leading to good stability.

To better understand the interaction between the Ni and B-vacancy, we performed an electronic structure analysis. We show the calculated Ni-3d and N-2p partial density of states in Figure 2b. We observed hybridization between these two states, due to the strong interaction between the Ni and the substrate.



Figure 1. Binding Energy (in eV) for transition metal embedded h-BN with B-vacancy (BM-BN) or N-vacancy (NM-BN).



Figure 2. (a) Schematic energy levels for geometries for the diffusion of a single Ni atom for two different paths. Barriers of 6.3 and 5.5 eV are observed. The initial state is labeled IS, the transition state is labeled TS, and the final state is labeled FS. (b) Partial density of states (PDOS) for the Ni-3d and N-2p states.

2.2. O₂, CO, O, and CO₂ Adsorption onto Sc, Cr, and Ni Atoms

To further understand the CO oxidation process, the adsorption of O_2 , CO, O, and CO_2 molecules on Sc, Cr, and Ni was investigated. O_2 , CO, and O molecules had a strong interaction with these materials at the metal site. The calculated adsorption energies for the most stable structures are summarized in Table 1. These structures are shown in Figure 3.

Substrate	Species	Adsorption Energy (eV)	Bond Length (Å)		Mulliken Charge of Adsorbed Molecules (e)
Sc-BN	O ₂	0.97	0-0	1.33	-0.43
	CO	0.63	C-O	1.14	0.07
	0	6.62	Sc-O	1.92	-0.55
	CO ₂	0.57	O-C-O	1.19, 1.17	0.03
Cr-BN	O ₂	2.47	0-0	1.43	-0.55
	CO	0.99	C-O	1.16	0.05
	0	6.18	Cr-O	1.60	-0.53
	CO ₂	0.36	O-C-O	1.19, 1.17	0.04
Ni-BN	O ₂	1.34	0-0	1.33	-0.27
	CO	1.23	C-O	1.17	0.25
	0	3.79	Ni-O	1.65	-0.44
	CO ₂	0.32	O-C-O	1.18, 1.17	0

Table 1. Optimized structures of adsorbed CO, O₂, O, and CO₂ molecules.

For Ti, V, and Mn, the CO_2 molecule would be strongly adsorbed, so these substrates may be poisoned and would not be good candidates for the catalysis of CO oxidation. For Sc, Cr, and Ni, CO_2 would be able to escape from the substrates, so these will be good candidates. The mixing between the Ni-3d and CO_2 -2p states was low near E_F (see Figure 3h), which was consistent with the weak interaction energy.

When a CO molecule is adsorbed onto the metal site, the most stable configuration has the CO adsorbed at a tilt (as shown in Figure 3a), with the carbon bonding to the Sc, Cr, or Ni sites. This result was very similar to the previous results on Co [32] and on Ag [33]-embedded h-BN. The calculated binding energies ranged from 0.63 eV for Sc to 1.23 eV for Ni. For CO on Ni, the CO bond lengths were 1.17 Å. These bond lengths were increased compared to the CO molecule by itself (1.13 Å). 0.25 |*e*| were transferred from the Ni to the CO. Therefore, the CO had a small positive charge. Positively charged CO molecules on metal SACs were also predicted for CO on Al–graphene [21] and on Co–BN [32]. On Sc and Cr, the adsorbed CO was also positively charged. We now discuss the PDOS. This showed that the mixing between the Ni-3d and CO-2p orbitals was relatively weak near the Fermi level. Weak mixing was also observed for Ru-BN [36].

When O_2 was adsorbed at the metal site, the best structure had two M–O bonds that lay parallel to the M-BN support (as shown in Figure 3c). The adsorption energies ranged from 1.0 to 2.4 eV (1.3 eV for Ni), which were larger than the corresponding CO absorption energies. The O-O bond length increased from 1.23 Å to 1.33 Å (on Sc and Ni) and 1.43 Å (on Cr), respectively. The O_2 had a charge -0.27|e|. On Sc and Cr, the adsorbed O_2 was even more negatively charged. This suggested that these systems may have acted as electron donors for the electrophilic O_2 , which could help promote O_2 activation. The hybridization between the Ni-3d and the O_2 -2p states (see Figure 3d) was stronger than that for CO adsorption near E_F (due to the higher binding energy). Therefore, O_2 could be activated easily by the Ni SAC. A nearby CO molecule could then react with the O_2 to ultimately produce CO_2 . This suggested that the Ni-BN SAC may be good for the catalysis of CO oxidation.

Next, we considered the adsorption of atomic O onto the Sc, Cr, and Ni metal sites. The optimized geometry is shown in Figure 3e. Atomic O had strong binding energies of 2.6, 6.2, and 3.8 eV on Sc, Cr, and Ni. The length of the M-O bonds ranged from 1.6 to 1.9 Å. From Figure 3f, we observed that the O-2p states overlapped with the Ni-3d states. This reflected the strong hybridization in this case and indicated that atomic O would have high oxidation activity.



Figure 3. Optimized geometric structures and PDOS for the adsorbed CO (a,b), O₂ (c,d),O (e,f),and CO₂ (g,h).

We show the frontier orbitals of CO, O_2 , O, and CO_2 on Ni in Figure 4. The HOMO and LUMO are shown. For CO, we observed significant hybridization between the Ni-3d and the CO- $2\pi^*$ states of the CO in the HOMO-1 and HOMO-2. The Ni contribution to the HOMO was dominated by the Ni d_p orbital. For O₂, there was slight mixing between the O₂- $2\pi^*$ and the Ni-3d states in the HOMO. The O-2p and Ni-3d also overlapped. These results clarified the detailed molecular orbital interactions for CO, O₂, and O on Ni-BN. In contrast, there was virtually no orbital interaction between CO₂ and Ni-BN. This was consistent with the fact that CO₂ had very low interaction energy with Ni-BN. Therefore, CO₂ could easily escape from the substrate.

The adsorption energies of the reactants on the substrates suggested a competition between CO and O_2 adsorption at the Sc and Ni. For Cr-BN, O_2 was likely to be adsorbed on the Cr atom sites, which allowed reactions with additional CO molecules from additional Eley–Rideal (ER) steps. For Ni-BN, the strength of the CO and O_2 adsorption was similar. Therefore, several processes were investigated below.



Figure 4. The frontier highest occupied molecular orbitals HOMO-2, HOMO-1, HOMO, and lowest unoccupied molecular orbitals (LUMO) for CO, O_2 , O, and CO_2 on Ni at the Γ -point. B atoms are beige, N atoms are blue, C atoms are gray, O atoms are red. The molecular orbitals are plotted in blue and yellow. The adsorbed molecules are located slightly above the plane.

2.3. Reaction Mechanism of CO Oxidation

The reaction process for single atom catalysts often includes a series of adsorption and desorption steps. The reaction barriers determine the catalytic efficiency. The traditional mechanisms of CO oxidation

include the Eley–Rideal (ER) and the Langmuir–Hinshelwood (LH) processes [32,35]. In the ER scheme, a preadsorbed O_2 molecule is activated by the support (in our case, M-BN, see Figure 5a). In the first stage, the O_2 interacts with a free gas-phase CO to form a bound CO_3 intermediate state. The result of the first stage is a single free CO_2 product, and a remaining single atomic O bound to the catalyst. The catalyst facilitates the dissociation of the O_2 at the catalyst site. In the second stage (see Figure 5b), the remaining adsorbed atomic O reacts with another free CO to create another CO_2 product (which desorbs).



Figure 5. Reaction energies with associated geometries for CO oxidation via the Eley–Rideal (ER) process for (**a**) Ni-BN first stage, (**b**) Ni-BN second stage, and (**c**) Cr–BN both stages.

The LH process begins with the co-adsorption of O_2 and CO molecules on the support. This is followed by the creation of an O–C–O–O intermediate state, which is peroxide-like (see Figure 6). In the first stage, a CO₂ molecule is desorbed. In the 2nd stage, atomic O interacts with a CO molecule to create a second CO₂ which is desorbed.

A new, more complicated CO oxidation process has recently been found. Yang et al. have described this termolecular Eley–Rideal process [30]. In this case, we started with two molecules located on the substrate. In our case, two CO were located on the Ni-BN substrate (see Figure 7). A free O_2 was activated and reacted with the two adsorbed molecules to create an intermediate state OCO–Ni–OCO. This state could then lead to the release of two CO₂ molecules.



Figure 6. Reaction energies with associated geometries in the LH process for CO oxidation on Ni. O₂ and CO are co-adsorbed on the support, and have come together to form a peroxide like intermediate IS1. (a) First stage of LH process. (b) Second stage of LH process.



Figure 7. Reaction energies for the Termolecular Eley-Rideal (TER) process of CO oxidation on Ni-BN.

2.4. ER Process

We first discuss the Eley–Rideal pathway to oxidize CO on Ni-BN. We present the potential-energy diagram and the geometries of the initial state, intermediate states, transition states, and products in Figure 5. We started with the O_2 adsorbed on the Ni catalyst site. Moreover, the CO was located relatively close to the O_2 , but not significantly interacting. This was the initial state (IS1). When the CO approached the bound O_2 , the O_2 bond could break to form two new C–O bonds, and an intermediate state (MS1) was formed. This step had a 0.9 eV barrier, with 3.5 eV net exothermic energy. Then, the carbonate-like intermediate state (MS1) could dissociate into a free molecule of CO_2 and an O atom bound to the Ni. This involved breaking one C-O bond, with barrier 1.2 eV, and 0.8 eV net endothermic reaction energy ($E_{reaction}$). At room temperature, the newly created CO_2 could be released as product. The E_{ads} value of CO_2 was 0.26 eV in the FS1 structure, very low. Owing to the rather weak adsorption energy, and the long distance to the substrate, the CO_2 product could be easily released. In the second stage, another CO molecule could approach and react with the bound O (IS2 in Figure 5b) to form a second CO_2 molecule. This second molecule could also escape as product. This step had a small 0.08 eV barrier, and exothermic $E_{reaction} = 3.0$ eV. The rate-limiting step of this ER process was in stage 1 in the creation of CO_2 from the intermediate state and had barrier 1.2 eV, which was relatively large.

In Figure 5c, we show the geometries and energies for the intermediate states for the ER oxidation of CO on Cr. The initial state was O_2 adsorbed on the Cr site. One CO molecule reacted with the O_2 , causing the O-O bond to break in the transition state (TS1). Then, a CO_2 molecule could form with a small 0.1 eV barrier, and a large exothermic $E_{\text{reaction}} = 3.9$ eV. Subsequently, a second CO could interact with the remaining bound oxygen (IS2) to create another CO_2 molecule which could desorb. This step had a large 1.3 eV reaction barrier (TS2). Considering the alternative case of Sc, the intermediate states of CO and O_2 could not easily dissociate into free CO_2 molecules, so the ER process could not be active in this case.

2.5. LH Process

The reaction pathway of CO oxidation via the LH process is displayed in Figure 6. In this case, the CO and O₂ co-adsorbed onto the metal atom. These could then react to form a peroxide-like intermediate. This state was selected as the initial state (IS1). Then, one oxygen atom of the O₂ molecule approached the CO molecule to form the intermediate state MS1. This step had a 0.09 eV reaction barrier, and an exothermic $E_{reaction} = 0.56$ eV. This state was peroxide-like. MS1 could continue forward to create one O on the surface and one CO₂ into the gas phase with a reaction barrier of 0.44 eV. One O was left on the Ni site with a Ni–O bond of 1.65 Å. This O could then join a CO molecule to create a second free CO₂. For the entire process, a 0.44 eV barrier was found for the rate limiting step OOCO(ad) \rightarrow CO₂(gas) + O(ad). As a result of the weak binding between the CO₂ and the catalytic site, product CO₂ molecules could be spontaneously released. This formed a complete cycle and then the system was ready for another round of catalysis. Note that CO and O₂ cannot easily be co-adsorbed on Cr and Sc, so the LH process will not be active for these metals. This low reaction barrier would allow rapid catalytic activity due to the significant exothermic $E_{reaction} = 2.30$ eV.

2.6. TER Process

A new three-molecule process was recently reported for single Au catalytic sites in h-BN [30]. After that, the TER process for CO oxidation was also found to occur on single Co [32] and Pd [35] catalytic sites in h-BN. Reaction energies for the TER process for Ni are shown in Figure 7. The first step involves two CO molecules bound to a catalytic Ni site. Then, a free O₂ approaches the two co-adsorbed CO molecules, which creates an OCO–Ni–OCO state (MS state in Figure 7). This step had a 0.47 eV reaction barrier, with an exothermic $E_{reaction} = 0.50$ eV. This state also had an unusual pentagonal structure. In this state, we observed an increase in the O-O bond length to 1.50 Å. In the next step, the O-O bond would be broken and two CO₂ molecules were created on the surface. These two CO₂ molecules only had a 0.32 eV binding energy, and so they could move into the gas phase. This step

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had a large exothermic $E_{reaction} = 5.30$ eV. This formed a complete cycle. This process was 2CO(ad) + $O_2 \rightarrow OCO$ -Ni-OCO(ad) $\rightarrow 2CO_2$ (gas). The conversion of O_2 to OCO-Ni-OCO dominated the reaction rate, and this had a barrier of 0.47 eV. We note that in the first step, the adsorbed CO had a positive charge. This may help promote O_2 activation [30]. Two CO molecules are not typically co-adsorbed on Sc-BN under normal conditions, so the TER process will not be active for Sc.

In summary, the energy barrier of the rate-limiting step for the LH process was dramatically lower than that for the ER process (0.44 eV vs. 1.23 eV) and just a little lower than that for the TER process (0.44 vs. 0.47 eV). Therefore, the LH process and the TER process (CO-promoted O_2 activation) were predicted to be dominant. The difference between the adsorption energy of CO (1.23 eV) and that of O_2 (1.34 eV) may not be significant. Preadsorption or exposure to CO or O_2 could determine the concentration of CO and O_2 on the surface.

2.7. Effect of Temperature and Entropy

We considered the effects of temperature and entropy on the reaction thermodynamics in the ER, LH, and TER processes. The change in the Gibbs free energy is:

$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$

In the above formula, ΔG is the difference between two successive steps of the reaction mechanism. ΔE is the difference in total energy directly obtained from DFT calculations at 0 K and $\Delta EZPE$ is energy in zero-point vibrational energy. T is the temperature. ΔS is the entropy change and is defined by ΔS = $\Delta S_{vib} + \Delta S_{rot} + \Delta S_{trans}$, where ΔS_{vib} , ΔS_{rot} , ΔS_{trans} are the contributions of vibrational, rotational, and translational modes, respectively.

For all three processes, ΔG was changing very slightly. For the ER process, the barrier for IS1 \rightarrow TS1 was 0.05 eV, for MS1 \rightarrow TS2 was 0.04 eV. The barrier for IS2 \rightarrow TS3 was 0.01 eV (all at 298 K). For the LH process, the barrier was 0 eV for IS \rightarrow TS1, and 0.01eV for MS \rightarrow TS2. The barrier in the TER process was 0.02 eV for IS \rightarrow TS1, and 0 eV for MS \rightarrow TS2 (all at 298 K). These values were small, and did not change much as the temperature was raised to 500 K.

We could make a rough order of magnitude estimate of the rates of the reaction using the Arrhenius relationship. The reaction time for each step is roughly:

$$\tau = \frac{1}{\nu e^{(\frac{-Ea}{\kappa_B T})}}$$

where E_a is the activation energy of the reaction, κ_B is Boltzmann's constant (8.617 × 10⁻⁵ eV/K), and ν is the attempt frequency, which is estimated to be on the order of 10¹² Hz. At three representative temperatures (298, 400, 500 K), the estimated reaction times are shown at Table 2. For the ER process, the reaction time of each elementary step was estimated to be $\tau = 2 \times 10^3$, 6×10^8 , and 2×10^{-11} s. For the LH process, IS1 \rightarrow MS1, MS1 \rightarrow FS1, and IS2 \rightarrow FS2 had times $\tau = 3 \times 10^{-11}$, 3×10^{-5} , and 2×10^{-11} s. For the TER process, the reaction times were 9×10^{-5} and 4×10^{-7} s, respectively (the TER analysis should also include the reactant concentrations for a more accurate estimate).

Table 2. Estimated reaction times for steps in the ER, LH, and TER processes at 298, 400, and 500 K.

	Step										
Reaction Time	ER			LH			TER				
	IS1-MS1	MS1-FS1	IS2-FS2	IS1-MS1	MS1-FS1	IS2-FS2	IS1-MS1	MS1-FS1			
τ (s) at 298K	2×10^3	6×10^8	2×10^{-11}	3×10^{-11}	2×10^{-5}	2×10^{-11}	9×10^{-5}	4×10^{-7}			
au (s) at 400K	0.2	3×10^{3}	1×10^{-11}	1×10^{-11}	4×10^{-7}	1×10^{-11}	8×10^{-7}	1×10^{-8}			
au (s) at 500K	0	2.5	6×10^{-12}	8×10^{-12}	3×10^{-8}	6×10^{-12}	5×10^{-8}	2×10^{-9}			

From the Arrhenius analysis, we concluded that the Ni SAC could operate at relatively low temperatures in the LH and TER processes. For the LH process, MS1 \rightarrow FS1 was the rate determining step. For the TER process, IS1 \rightarrow MS1 was the rate determining step. All reactions became faster as the temperature was increased.

3. Computational Methods

We used the same general computational methods as in our previous work [26]. This method was shown to be satisfactory for these calculations in our previous work. We used the Dmol³ program in Materials Studio 2016 [37]. Spin-polarized DFT-D calculations were carried out using the Dmol³ package [37], which is part of Materials Studio 2016 (Accelrys, San Diego, CA, USA). The generalized gradient approximation using the PBE functional [38] with long-range dispersion correction via the Tkatchenko–Scheffler scheme [39] was used. We employed the DFT semi-core pseudopotentials (DSPP) [37], which replaces core electrons by a single effective potential to describe the core–valence interactions with some relativistic corrections. We used the double numerical plus polarization (DNP) basis set with a "fine" orbital cutoff. During the geometrical optimization, the convergence tolerances were set to 10^{-5} Ha for the energy, 0.002 Ha/Å for the force, and 0.005 Å for the displacement. The electronic self consistent field tolerance was set to 10^{-6} Ha. We estimated the total error in the binding energies and energy barriers to be 0.1 eV [26]. A Fermi smearing parameter of 0.003 Ha was used in the calculations to achieve quick and accurate electronic convergences.

The reciprocal space was sampled with a $(4 \times 4 \times 1)$ k-point grid generated automatically using the Monkhorst–Pack method for the relaxation calculations. Complete linear synchronous transit (LST)/quadratic synchronous transit (QST) calculations were performed to locate the transition states (TS). Moreover, the transition states were confirmed with frequency calculations by the number of imaginary frequencies (NIMG) with NIMG = 1.

The calculated lattice constant of h-BN was 2.51 Å with a B–N bond length of 1.45 Å. This was consistent with a previous work [31]. A $6 \times 6 \times 1$ supercell of h-BN containing 72 atoms was used as a support. A single transition metal atom substituted a B or N atom. DMol3 was set to auto to find the correct spin state in the unrestricted calculations. The thickness of the vacuum layer was more than 15 Å to avoid interlayer interactions. The adsorption energy (E_{ads}) was determined using:

$$E_{ads} = (E_{adsorbate} + E_{support}) - E_{adsorbate/support}$$

 $E_{adsorbate}$, $E_{support}$, and $E_{adsorbate/support}$ are the total energies of the free adsorbate, the support, and the support with the adsorbate. All three energies were derived from calculations using the same periodic dimensions and the same computational settings. A positive value indicates an exothermic adsorption.

4. Conclusions

In this work, we studied h-BN nanosheets with individual TM metal (Sc, Ti, V, Cr, Mn and Ni) catalytic sites located at defects using DFT-D calculations. After studying the adsorption of reactants and products, we decided to focus on Sc, Cr, and Ni. We considered the detailed processes of CO catalytic oxidation to CO₂ on Ni. The ER, LH, and the new TER processes were evaluated. Sc did not readily catalyze CO oxidation. Cr catalyzed CO oxidation with the ER process, although the CO + O (ad) \rightarrow CO₂(gas) step has a large 1.3 eV barrier. For the Ni catalyst, the MS1 to TS2 step dominated the formation of CO₂ in the ER process (1.2 eV barrier). For the Ni LH process, the OOCO(ad) \rightarrow CO₂(gas) + O(ad) step determined the reaction rate with a low 0.44 eV barrier. For the Ni TER process, the activation of O₂ to the OCO–Ni–OCO intermediate was the rate determining step with a low 0.47 eV barrier. We concluded that the proposed Ni-BN materials should be stable and active catalysts between 300 and 500 K.

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