Catalytic effect of TMCmHm compounds on the reaction rate of " Hydrazin - Oxygen "fuel cell "TM = Cr, Sc, Ti, V and m= 4 or 5" A DFT Study

Zohreh Mohammadi Ahmad Mahmodi
Islamic Azad University

Mehran Aghaie (✉ marmin20042000@yahoo.com)
Islamic Azad University   https://orcid.org/0000-0001-7393-6043

Maziar Noei
Islamic Azad University

Hossein Aghaie
Islamic Azad University

Abstract

Platinum and similar metals are suitable catalysts in response to fuel cells, however, because of being costly, their use is limited. So in this study, the catalytic efficiency of some organometallic compounds with the general formula TMCmHm on the reaction rate of "Hydrazine- Oxygen "fuel cell was studied via density Functional Theory (DFT). To perform the respect calculations, the PW91 method and 6-31 G(d) basis set were used. Bonds' length of O=O and N-N increased in response to their adsorption onto TMC_mH_m and theoretical study of N_2H_4-O_2 fuel cell the partial transfer of negative charge from organometallic compounds to their π * orbitals. Bond length of O=O increased by 24% due to its adsorption on ScC_5H_5 and N-N on ScC_5H_5 increased by 11%. The optimal structure of each studied organometallic compound was plotted by performing natural bond orbital calculations (NBO). The energy of the highest occupied molecular orbital (EHOMO) and the lowest unoccupied molecular orbital (ELUMO) were calculated. Besides, , the gap energies (Eg), chemical hardness (⍵), chemical potential (μ), and electrophilicity (ω) were calculated in each case. Then, the optimal structure of O2/TMCmHm and N2H4/ TMCmHm pairs was plotted; the adsorption energy of O2 and N2H4 on each of TMCmHm was evaluated. The kinetic adsorption of O2 and N2H4 on the Sc C5H5 compound was investigated by the 6-31 G * method. The potential energy of O2/TMCmHm and N2H4/ TMCmHm pairs in the initial and final position and the transient state were estimated, and the respect kinetic parameters were calculated.

Introduction

Fuel cells play an essential role in supplying green energy by converting chemical energy into high-efficiency electrical energy (nearly 90%) [1,2]. Today, fuel cells are used in various fields such as electrical energy,production hybrid cars, spacecraft, military submarines, power plants, etc. [3,4] The main problem in the practical application of fuel cells is the slowness of the anode and cathode half-reactions in them as well as the high economic costs of using platinum as a catalyst [5]. Since the introduction of fuel cells, many studies have been done to increase the reaction rate in them using various catalysts [6-12] . To enhance the rate of the cathode and anode half-reactions in fuel cells, pure platinum and other expensive metals in pure or composite forms have been used extensively [13,14]. Nevertheless, the use of these metals is limited due to their high cost [14]. In this regard, the use of organometallic compounds containing Transition Metals as low-cost catalysts has been considered by some researchers in the field of computational chemistry and has offered valuable results (15-19).

Organometallic compounds are very diverse and have many uses. There is at least one carbon-metal bond in each organometallic compound[20]. This bond may be ionic, covalent, or coordinate covalent. In some organometallic compounds, there is no direct bond between carbon and metal, but ligands with dative carbon structures share electron pairs with metal ions to occupy valance layer orbitals of the transition metal, where the intended organic metal compount reaches its stable electronic structure [21, 22] . The ns, np, and, nd transition metal valance layer orbitals are involved in the intended organometallic compound, with the metal appearing as both an electron donor and an electron acceptor. In this way, the rule of 18 electrons is established for the transition metal valance layer with the

organometallic compound achieving significant stability. Metallocenes are an important class of organometallic compounds containing transition metals. Their general formula is $M(C_5H_5)_2$ (M is a transition metalion). Ferrocene ($Fe(C_5H_5)_2$) is the head of the metallocene group. Most metallocenes have high thermal stability. The melting and boiling points of ferrocene are 174 and 249^0C, respectively [23-26].

Metallocenes have many applications. They are used as inexpensive catalysts in many industrial and functional reactions. In addition, they have been used on a large scale in pharmaceutical treatments, in reducing the viscosity of industrial oils, in the preparation of semiconductors, in the petrochemical industry as well as oil and gasoline refining, *etc.*[27]. Metallocenes are somewhat unstable against thermodynamic oxidation, though this instability is compensated by their remarkable kinetic stability under normal conditions. As a result, under normal conditions, they can be safely used as cheap and effective catalysts in various reactions, especially in fuel cells [28-31]. metallocenes are also relatively stable in the presence of oxygen (under normal conditions). Thus, they can be used as catalysts in the cathodic reduction of O_2 in fuel cells. Much experimental and theoretical research has been done to find inexpensive and efficient catalysts. Recently, significant computational studies based on (DFT) have been performed to activate oxygen in the cathode via various catalysts [32, 33].

In this study the catalytic role of each of the studied organometallic compounds in the activation of O_2 in the cathode and N_2H_4 anode of "N_2H_4 - O_2" fuel cell was studied by the DFT method. For this purpose, the intended structures were optimized for which density of state (DOS) diagrams were drawn. The energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LOMO}) were also calculated. Gap energy (E_g), chemical hardness (⬚), and chemical potential were calculated for each organometallic compound. Using the optimal energy of the structures used, the adsorption energy (E_{ad}) of each of the "adsorbent-adsorbate" systems was also calculated on which the necessary analyses were performed. The results revealed that the organometallics of transition metals used have an effective catalytic role in enhancing the reactivity of O_2 in the cathode and N_2H_4 in the anode of "N_2H_4 - O_2",fuel cell with the catalytic role of Sc C_5H_5 being more pronounced than that of other organometallics used.

Computational Details

Calculations were performed by DFT method at PW91 level and base series 6-31 (d). The optimal structure of each TMC_mH_m was plotted by NBO calculations. Density of State diagrams (DOS) were plotted by Guassum software for optimized structures. Using the above diagrams, the energy of the highest occupied molecular orbital (E_{HOMO}) and the energy of the lowest unoccupied molecular orbital (E_{LUMO}) were calculated for each of the organic metal compounds used. Using these energies, the gap energy (E_g) was estimated for each organic metal compound. .In addition, the chemical hardness (⬚), chemical potential (μ) and electrophilicity (ω) were calculated for each of them.Afterward, the optimal structure of each R / OM pair was plotted and its energy was evaluated in the same way as earlier (R is

O2 or N_2H_4 and OM delivers a studied organometallic). The adsorption energy (E_{ad}) for each "adsorbent-adsorbate " (R / OM) pair was calculated from Equation (5). The bond elongation of O = O and N-N in response to their adsorption on TMC_mH_m were estimated; it was found that their elongation compared to the pre-adsorption state was 24% and 11%, respectively. The increase in the bond lengths is due to the transfer of some negative electric charge from the organometallic compound to their π * orbitals. From the calculations performed, it was found that the TM atom in the studied organometallics has gained some negative electric charge. Next, to evaluate the adsorption kinetics of O2 and N_2H_4 on to the ScC_5H_5 compound ,the 6-31G * and the PW91 methods were msed and the change of potential energy of each pair of O_2/ScC_5H_5 and N_2H_4/ScC_5H_5 systems in terms of reaction coordinate (bond length of O=O or N-N in N_2H_4 were evaluated and the respect plots were drawn. The theoretical calculation showed that for every pair (O_2/ScC_5H_5 or N_2H_4/ScC_5H_5) exit only one transition state(TS). Using the above calculations, the potential energy of the initial state and the final state of the "adsorbent-adsorbate" system and as well as the transition state in each case were estimated, through which it was possible to estimate the activation energies and the change in the potential energy of the adsorption process. NBO calculations brought about the estimation of the negative electric charge on the TM atom in TMC_mH_m. In addition, the amount of charge transfer from them to O2 and N_2H_4 adsorbed on them was also estimated.

$$E_g = E_{LUMO} - E_{HOMO} \qquad (1)$$

$$⬜ = \tfrac{1}{2}(E_{LUMO} - E_{HOMO}) \qquad (2)$$

$$\mu = \tfrac{1}{2}(E_{LUMO} + E_{HOMO}) \qquad (3)$$

$$\omega = \mu^2 / 2⬜ \qquad (4)$$

$$E_{ad} = E_{R/OM} - (E_R + E_{OM}) \qquad (5)$$

Results And Discussion

The optimal structure of each of the studied TMC_mH_m was drawn after its optimization of each organometallic compound such as TMC_4H_4 or TMC_5H_5 (Fig. 1). These structures included CrC_4H_4, CrC_5H_5, ScC_4H_4, ScC_5H_5, TiC_4H_4, TiC_5H_5, VC_4H_4, and VC_5H_5. The TM-C bond lengths were optimally 1.99 Å, 2.12 Å, 2.14 Å, 2.27 Å in TMC4H4 and 1.99 Å, 2.46 Å, 2.32 Å and, 2.02 Å in TMC_5H_5, respectively. The mentioned lengths were changed after. molecules on them, which will be examined in the following NBO calculations showed that the TM atom has a small amount of negative electric charge in each of the TMC_mH_m studied (Table 1). Hence, when O_2 and N_2H_4 come in contact with them, some negative charge would be sent from the TMs to the O=O and N-N bonds. As a result of this charge transfer, these bonds become significantly elongated and unstable, and their chemical affinity for participation in the cathode and anode half-reactions in oxygen-hydrazine fuel cell will be increased, respectively and the most important result would be an increase in the reaction rate of the cell in question.

The amount of negative electric charge accumulated on the TM atom lied in the range of 0.489 to 0.835au in TMC$_4$H$_{4s}$ and in the range of 0.485 to 0.879au in TMC$_5$H$_5$ (Table 1) (au stands for the basic unit of electric charge, the charge of an electron). Thus, Sc has gained the most negative charge in TMC$_5$H$_5$ and can therefore emit more negative charge to the O2 and N$_2$H$_4$ adsorbed on it, and increasing their chemical affinity for participation in the half-reaction of cathode and anode of the "oxygen-hydrazine" cell, respectively. This ability is lower in other studied organometallics.

The diagram of the density of state was plotted for each of the optimized structures upon these diagram,the estimation of E$_{HOMO}$ and E$_{LUMO}$ were done for each structure. Fig. 2 displays two examples of them related to ScC$_4$H$_4$ and ScC$_5$H$_5$. Using the intended E$_{HOMO}$ and E$_{LUMO}$, the gap energy (Eg) was calculated according to Equation (1) in each case (Table 1). ▯, μ, and ω were calculated according to Equations 2 to 4 in each case as reported in Table 1 As can be seen from the data in Table 1, ScC$_5$H$_5$ has the lowest E$_g$ (0.24eV). Thus, it can be concluded that the chemical affinity of ScC$_5$H$_5$ for participating in the intended processes would be higher than that of the other studied organometallics and lower in Vc$_5$H$_5$ than in the others.

Table 1 Electric charge on TM in TMC$_m$H$_m$ in terms of electron charge as elementary unit of charge (au), E$_g$, ▯, μ, and ω in terms of electron volt (eV)

Structure	-charge	E$_g$			Ω
CrC$_4$H$_4$	0.483	2.44	1.22	-2.820	3.26
CrC$_5$H$_5$	0.485	1.30	0.65	-2.850	6.25
ScC$_4$H$_4$	0.835	0.52	0.26	-3.080	18.24
ScC$_5$H$_5$	0.879	0.24	0.12	-2.815	32.90
TiC$_4$H$_4$	0.772	0.90	0.45	-3.090	10.61
TiC$_5$H$_5$	0.766	0.96	0.48	-2.960	9.13
VC$_4$H$_4$	0.527	0.70	0.38	-3.505	17.50
VC$_5$H$_5$	0.453	1.24	0.62	-3.572	10.27

Looking at Table 1, it can be seen that the chemical hardness of ScC$_5$H$_5$ is smaller than that of the others. As chemical hardness is a measure of a molecule's resistance to breakage, as well as a measure of its chemical affinity for chemical reactions, ScC$_5$H$_5$ is more capable of destabilizing the O$_2$ and N$_2$H$_4$

adsorbed on it. As a suitable and effective catalyst, it can be well used in the structure of anode and cathode of "oxygen-hydrazine" fuel cell to boost the rate of these half-reactions.

Considering the values collected in Table 1, it can be easily concluded that the changes trund of , E_g , $\boxtimes$ and,μ in relation to the studied TMC_mH_m and the resulted conclusions are well consistent with each other. For example, every one of electric charge ,E_g , $\boxtimes$ and,μ associated with ScC_5H_5 indicates that the mentioned compound has a higher chemical affinity and is more capable of destabilizing the adsorbed O_2 and N_2H_4. To better illustrate the above consistency,

To evaluate the adsorption process of O_2 on each of the TMC_mH_m, it was placed at a suitable distance from each of them after which the optimal structure of each pair of O_2/ TMC_mH_m was drawn based on the previous method (Fig. 3) and then the bond length of O=O and TM-C in each pair were determined under optimal conditions where, the value of each of which has been inserted in Fig. 3 on the intended optimal structure. Comparison of bond length of O=O in adsorption conditions and in free conditions (1.210 Å) showed that the mentioned length increased due to the adsorption process. This rise in the bond length destabilizes adsorbed O_2 and enhances its reactivity. Thus, using the studied organometallic compounds in the cathode structure of "oxygen-hydrazine" cell can increase the activity and reactivity of O_2 in the cathode of the cell and enhance the rate of O_2 reduction in the cathode of the cell. O_2 adsorption on ScC_5H_5 is associated with a greatest increase in the bond length O=O. Thus, the catalytic role of ScC_5H_5 in destabilizing O_2 and accelerating the cathode half-reaction in the "oxygen-hydrazine cell" is greater than that of other organometallics used.

Bond length of O=O in the non-adsorbed state is 1.210 Å [26]; while after adsorption on the studied organometallic compounds was increased as follows: in the O_2/CrC_4H_4 , O_2/ScC_4H_4 , O_2/TiC_4H_4 , $O_2/ VC4H4$ pairs reached to 1.48, 1.43, 1.48 ,1.49 Å, respectively, and for O_2/ CrC_5H_5 ,O_2/ ScC_5H_5, O_2/ TiC_5H_5, and $O_2/ V C_5H_5$ reached respectively to 1.47, 1.49, 1.48, 1.45 Å. Also, the bond length of TM-C was increased after O_2 adsorption on the used organometallic compounds ,e.g from 2.46 Å to 2.49 Å for Sc-C in ScC_5H_5. The adsorption energy (E_{ad}) of O_2 adsorbtion on to each of the studied TMC_mH_m was calculated using the optimized structures in Figure 4 and according to Equation (5) where the results are reported in Table 2. In the table, the negative electric charge transferred from TM in TMC_mH_m to adsorbed O_2 and the O=O bond length in the adsorbed state (($r (O_2)$)) have also been listed. As can be seen, the negative charge emitted to O_2 is higher in the O2 / ScC_5H_5 pair as an "adsorbent-adsorbate" system, which in turn causes a further increase them O=O bond length. The calculated O_2 adsorption energy on the ScC_5H_5 in turn is higher than the other adsorption energies (see Table 2). In conclusion, the ScC_5H_5 has a more pronounced catalytic role in the activation of O_2 to participate in the reduction half- reaction in oxygen-hydrazine fuel cell. Nevertheless, other organometallics used have also a relatively good catalytic role.

Table 2 Negative electric charge emitted on adsorbed O_2 in terms of electron charge as the elementary unit of charge (au), adsorption energy (E_{ad}) in terms of electron volts (eV) and bond length of adsorbed O_2 , $r_{(O2)}$)) in Å

Structure	-charge	E_{ad}	$r(O_2)_{ad}$
O_2/ CrC4H4	0.539	-6.05	1.430
O_2/ CrC$_5$H$_5$	0.584	-6.41	1.477
O_2/ ScC$_4$H$_4$	0.879	-7.39	1.492
O_2/ ScC$_5$H$_5$	0.899	-7.49	1.494
O_2/ TiC$_4$H$_4$	0.733	-7.34	1.487
O_2/ TiC$_5$H$_5$	0.697	-7.24	1.486
O_2/ VC$_4$H$_4$	0.629	-6.71	1.484
O_2/ VC$_5$H$_5$	0.540	-6.11	1.458

As can be seen from the results collected in Table II, in the O_2/ ScC$_5$H$_5$ pair, greatest charge is transferred from Sc to adsorbed O_2.Totally the charge transfer is within the range 0.539 - 0.879au for O_2/ TMC$_4$H$_4$ pairs; it is within 0.540 - 0.899au for O_2/ TMC$_5$H$_5$ pairs . Due to the higher negative charge transfer to O_2 in the O_2/ ScC$_5$H$_5$ pair, the adsorption energy is also higher in the mentioned pair. This indicates that the adsorption efficiencyof O_2 on ScC$_5$H$_5$ is higher than in other organometallics used. The increase in bond length O=O in response to the adsorption process is also greater in the ScC$_5$H$_5$ /O_2 system. The increase in bond length is associated with its instability and enhanced activity. Indeed, the results of E_{ad} calculations indicate that ScC$_5$H$_5$ can play a more catalytic role in increasing the cathodic half-reaction rate in " N_2H_4 − O2" cell than other studied organometallics. The comparison of catalytic role of the studied compounds is as follows:

CrC$_4$H$_4$<VC$_5$H$_5$<CrC$_5$H$_5$<VC$_4$H$_4$<TiC$_5$H$_5$<TiC$_4$H$_4$<ScC$_4$H$_4$< ScC$_5$H$_5$

The adsorption of N_2H_4 molecule on TMC$_m$H$_m$ was also evaluated according to the same method as adsorption of O_2 on them, the intended structures were optimized and the optimal structures were drawn (Fig. 4), with the repeated necessary calculations (Table 3). Here, some negative electric charge from TMs in TMC$_m$H$_m$ is also sent to the N-N bond in N_2H_4 and makes it unstable. This instability causes the N_2H_4 to participate more rapidly in the anodic oxidation of the "oxygen-hydrazine" cell. Here again, ScC$_5$H$_5$ has

a more pronounced catalytic role in increasing the reactivity of N_2H_4 in the anode of "oxygen-hydrazine" cell .

The adsorption energy of N_2H_4 on to each TMC_mH_m was calculated according to Equation (5) by considering the optimal structure of each pair of N_2H_4/ $TM - C_mH_m$ (Table 3). Here, the N_2H_4 adsorption energy on ScC_5H_5 is also more negative than the other adsorption energies, which is a good indication of the more pronounced catalytic efficiency of ScC_5H_5 compared to the other organometallics evaluated in this study.

The comparison of the charge magnited transfer from TMC_mH_m to N-N is as follows:

N_2H_4 / ScC5H5 > N_2H_4 / ScC_4H_4 > N_2H_4 / TiC_5H_5 > N_2H_4 / TiC_4H_4 > N_2H_4 / VC_5H_5 > N_2H_4 / VC_4H_4 > N_2H_4 / CrC5H5 > N_2H_4 / CrC_4H_4
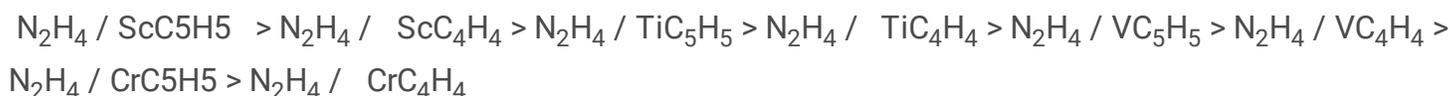
Table 3 Negative electrical charge transfer from TM in TMC_mH_m to adsorbed N_2H_4 in terms of (au), Adsorption energy (E_{ad}) in terms of (eV), N-N bond length adsorbed on TMC_mH_m in Å (TM = Cr, Sc , Ti, V) and (m = 4or5).

Structure	-Charge	E_{ad}	r(N-N)
N_2H_4/CrC_4H_4	0.168	-1.12	1.501
N_2H_4 /CrC_5H_5	0.210	-1.23	1.520
N_2H_4/ScC_4H_4	1.122	-2.31	1.583
N_2H_4/ ScC_5H_5	1.257	-2.91	1.599
N_2H_4/TiC_4H_4	0.843	-0.51	1.542
N_2H_4/TiC_5H_5	0.935	-0.27	1.545
N_2H_4/VC_4H_4	0.371	-2.12	1.572
N_2H_4/VC_5H_5	0.469	-2.17	1.581

The adsorption kinetics of each of O_2 and N_2H_4 on to the ScC_5H_5 compound were then studied using the 6-31G *method. For this purpose, the potential energy change diagram of the system including adsorbate (O_2 or N_2H_4) and adsorbent (ScC_5H_5) was plotted in terms of the reaction coordinate (bond length O=O or N-N in N_2H_4) while only one transition state was observed in each case. The potential energy of the "adsorbent-adsorbate" in the initial and final state and the potential energy of the transition state were estimated. Based on them, it was possible to estimate the activation energies of the forward and reverse processes and the change in the intended potential energy in each case. The results of the calculations and the estimated parameters are shown in Figs. 5 and 6. Accordingly, each of the studied adsorptions

would has a better advancement in the forward direction than in the reverse direction, where performing the studied adsorption processes is associated with a reduction in the potential energy. The potential energies of the O_2/ ScC_5H_5 pair in the initial position (E_1), in the transition state ($E_\#$), and in the final position (E_2) were calculated as 7.49,-7.02 and -7.73 eV respectively. The mentioned energies in relation to N_2H_4/ ScC_5H_5 pair were equal to -2.91, -2.13, and -3.44 eV, respectively.

Conclusion

The results of this study revealed that the gap energy, chemical hardness, and chemical potential of the studied organometallic compound are different and as such their resistance to breakage and their chemical activity plus reactivity will also be different. The gap energy for ScC_5H_5 was lower than that of the others, indicating that it had a higher reactivity than the rest of the studied organometallics. NBO calculations showed that the transition metal atom in TM C_mH_m had some negative electric charge, where this amount was higher in ScC_5H_5 than in the others. The calculated results indicated that TM C_mH_m can be selected as good adsorbent for adsorption of O_2 and N_2H_4. During the adsorption process, some negative electric charge was emitted from the TM's to O_2 or N_2H_4. This charge emission caused the bond lengths of O=O and N-N in N_2H_4 to stretch, causing their instability. Charge emission and instability by ScC_5H_5 were higher than by other organometallics used. The instability of O_2 and N_2H_4 in this way would increase their chemical activity and reactivity where they participate in the intended half reactions more easily. Thus, when such organometallics participate as an inexpensive catalyst in the cathode and anode structure of oxygen-hydrazine fuel cell, they will significantly increase the reaction rate of that cell. Among them, the catalytic role of ScC_5H_5 is more obvious. Calculations of adsorption O_2 and N_2H_4 on to TM C_mH_m showed that the adsorption energy was negative for all of them and in the case of ScC_5H_5 it was more negative than the others. This result confirms that ScC_5H_5 has a more suitable catalytic role compared to other TM C_mH_m used. Overall, it can be concluded that the studied TM C_mH_m have significant catalytic properties in destabilizing the O_2 and N_2H_4 adsorbed on to them. Thus, with their participation in the structure of the cathode and anode of "oxygen-hydrazine" fuel cell, the rate of cell reaction will be significantly increased. In addition, the catalytic properties of ScC_5H_5 are more dominant than those of the others, and the mentioned compounds can be considered as a cheap and completely effective catalysts in the "oxygen-hydrazine" cell reaction. The adsorption kinetics of each of O_2 and N_2H_4 on ScC_5H were theoretically and computationally studied with only one transition state observed for each of them. The results of calculations revealed that the activation energy of the adsorption process in the forward direction in each case was smaller than in the reverse direction, suggesting that the adsorption processes.Kinetically in a better situation in the forward direction than the reverse. It was also found that the adsorption process in each case was accompanied with a reduction in potential energy, which is considered energetically appropriate.

Declarations

Acknowledgment

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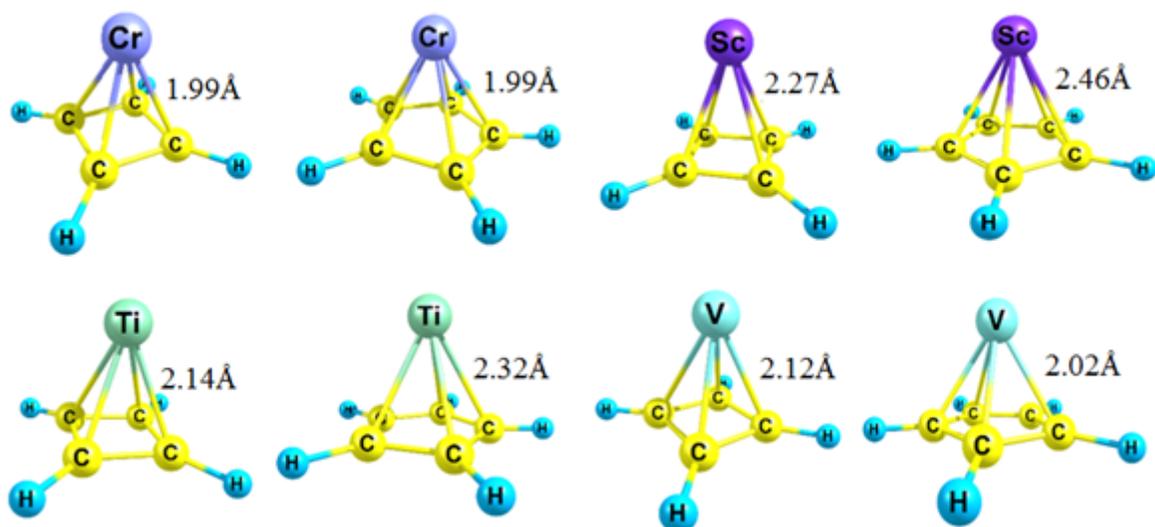
Figures

Figure 1

The optimized structure of each organometallic compound such as TM − CmHm, (TM = Cr, Sc , Ti, V) and (m = 4or5) with the bond length TM-C in each case listed on each structure.
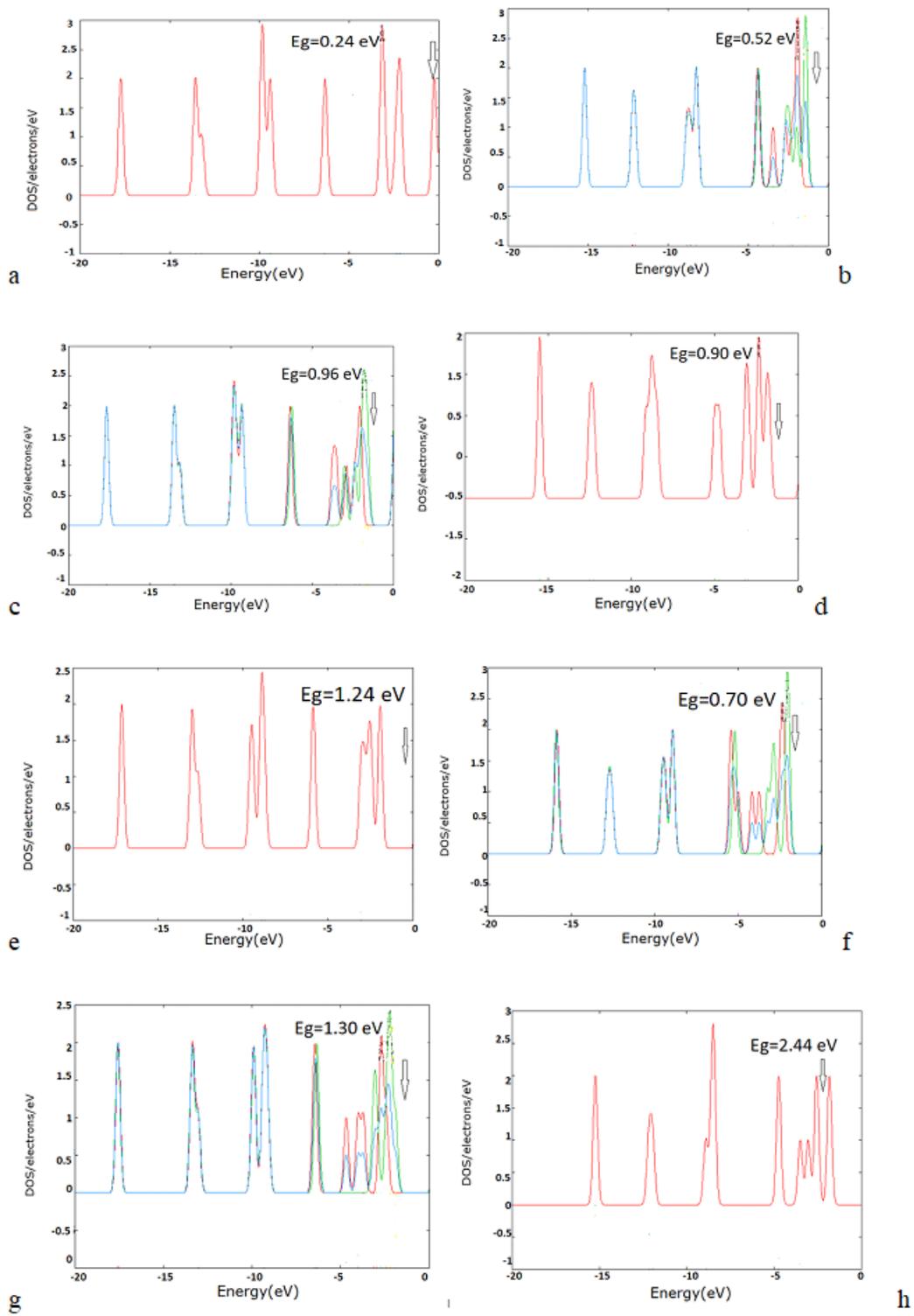
Figure 2

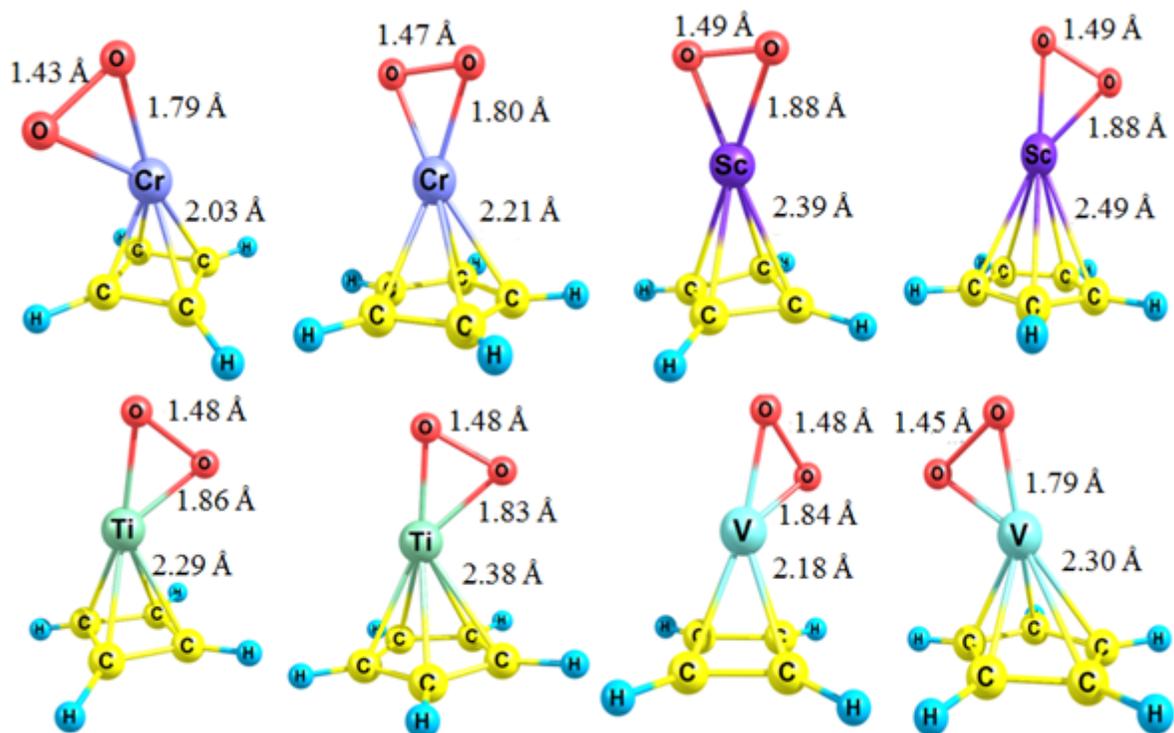Density of state (DOS) for a)ScC5H5 b)ScC4H4 c)TiC5H5 d) TiC4H4 e)VC5H5 f)VC4H4 g)CrC5H5 h) CrC4H4

Figure 3

Optimal structure of each of the O2/ TMCmHm pair ("absorbent-adsorbate" pair). Bond length O = O and bond length of each TM-C under adsorption conditions has been given on the intended structure in the figure (TM = Cr, Sc , Ti, V) and (m = 4or5) .
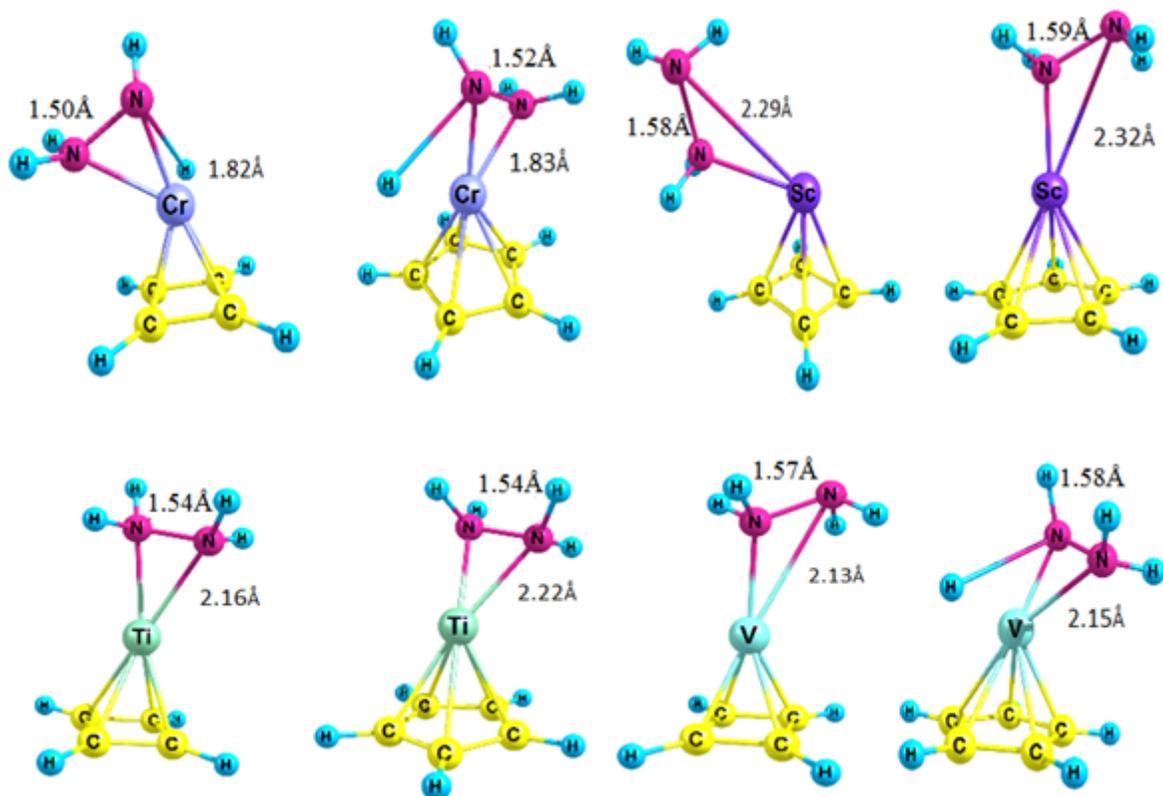
Figure 4

The optimized structures of "adsorbent-adsorbate" systems (N2H4/TM − CmHm). Other required bond lengths are also inserted on each structure in the figure (TM = Cr, Sc , Ti, V) and (m = 4or5).
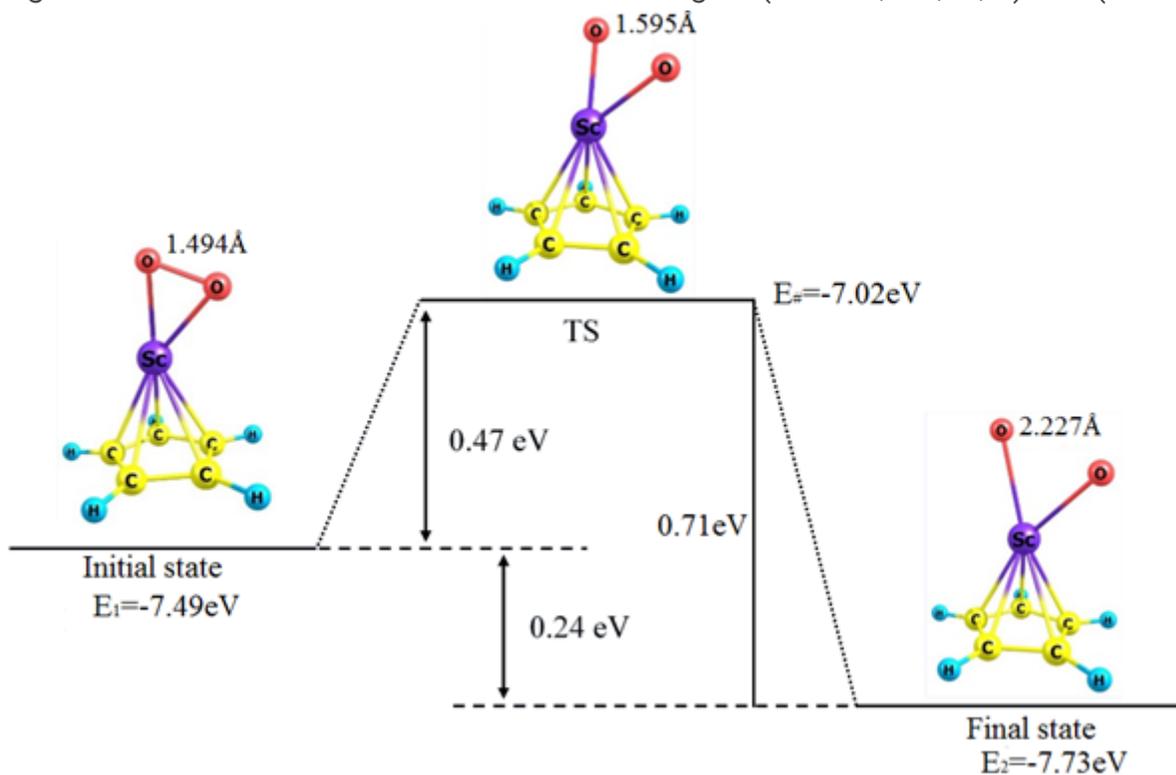

Figure 5

Diagram of potential energy change of O2 / ScC5H system in terms of bond length O=O. The forward and reverse activation energies and the potential energy change and the other required kinetic parameters are given in the diagram.
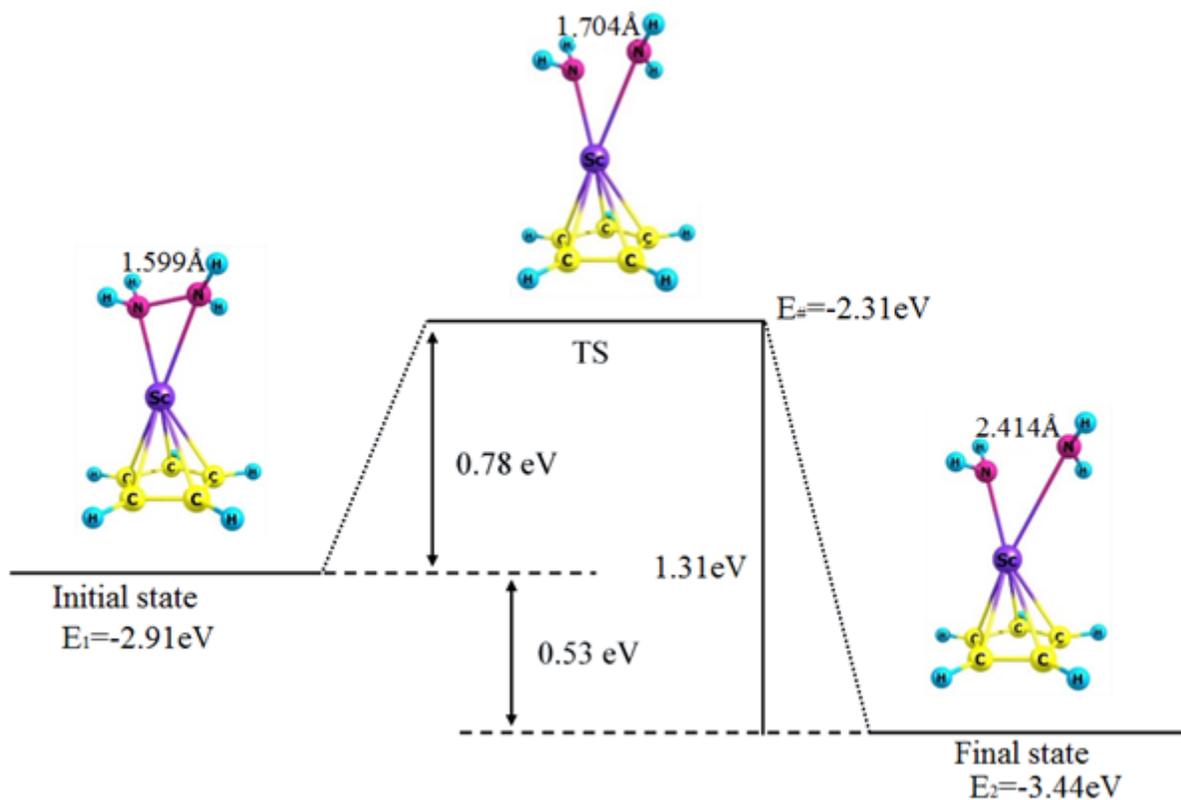
1.704Å

E₄=-2.31eV

TS

0.78 eV

1.599Å

0.78 eV

1.31eV

Initial state
E₁=-2.91eV

0.53 eV

2.414Å

Final state
E₂=-3.44eV

Figure 6

Diagram of potential energy change of the N2H4 / ScC5H5 system in terms of bond length N-N. The forward and reverse activation energies and the potential energy change and the other required kinetic parameters are given in the diagram.