A Density Functional Theory Study of CH_4 Disaggregation on Ni Catalyst

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Abstract

Based on ab initio calculation method and the quantum mechanics of first principles, the energy, structural change, charges population and orbital interaction of CH_4 continuous dehydrogenation process are calculated in this paper respectively. Results show that in four elementary reactions of CH_4 dehydrogenation, the activation energy maximization of CH ·dehydrogenation on Ni is a rate-determining step in the whole process of dehydrogenation. It is inferred that CH · free radicals may be enriched on the surface of Ni in great quantities, and Ni catalyst plays a role of donating electrons when catalyzing the dehydrogenation of CH_4.

Keywords

CH_4, Nickel, Catalyze, Density Functional Theory (DFT).

1. Introduction

Energy is an important material basis of human survival and development, and focus of today's international politics, economy, military affairs and diplomacy. Since the 1950s, lots of natural gas resources have been developed and the supply has been increased. In 2001, the world natural gas consumption reached 2.4046 trillion cubic meters, which accounted for more than 24% of the world's energy consumption structure. Moreover, natural gas is a kind of high-quality chemical materials, and about more than 50 countries have developed natural gas chemical industry in different degrees. Total annual global output of once-processed natural gas chemical industry products reaches 1.16 billion tons, and annual gas consumption is about 140 billion cubic meters. At the same time, natural gas is recognized as clean energy in the world today, whose pollution occupies 1/40 of the pollution from oil and 1/800 from the coal, and therefore it is widely used in industrial and civil fuel.

The main composition of natural gas is methane, whose content usually accounts for 83% ~ 99%, and therefore the methane conversion and utilization occupies a very important position in natural gas chemical industry. The activation of methane molecules is the basis of methane conversion and utilization; whatever the conversion is, methane activation is a must. As the simplest and the most stable alkane accounting for the biggest proportion, methane also has a lot of reference and guiding significance for the activation of other inert molecules. Therefore, methane activation has become the most challenging subject at the forefront.

This paper has made an in-depth research on the related foundation of methane activation; through quantum chemistry calculation of direct disaggregation process of methane under the catalytic systems of single atom Ni, the direct conversion and utilization of methane has made a breakthrough.

2. Research Methods and Models

In this paper, the quantum mechanics calculation adopts ab initio calculation method which is based on first principles. The calculation is conducted through density functional theory (DFT)[7, 8] module DMol^3 [9-11] in the software of Materials Studio developed by Accelrys[5, 6] company. The wave function in DMol^3 module is expanded in the form of DNP (double-numeric quality) basis set. Density functional theory calculations use GGA[12] (generalized gradient approximation) of PBE[13] (Perdew-Burke-Ernzerhof) functional, and the absolute error is usually within 0.2eV[14, 15]. Convergence tolerance is: energy Ha (1Ha=2625.5kJ·mol^{-1}), the force field 0.002Ha/Å(1Å=0.1nm), displacement 0.005Å. The convergence tolerance of self-consistent field is 1×10^{-6}; the density's multipole expansion adopts Octupole, and the electronic structure is obtained under the condition of spin without limitation by solving the Kohn-Sham equation. Transition state search uses LST/QST (Linear Synchronous Transit/Quadratic Synchronous Transit) method for calculation.

Reaction enthalpy change ΔH, such as A+B=C+D, calculated through the following formula:

$$\Delta H=[E_{(C/catalyst)}+E_{(D/catalyst)}]-[E_{(A/catalyst)}+E_{(B/catalyst)}],$$

Therein, $E_{(C/calalyst)}$ and $E_{(D/catalyst)}$ is the total energy of Ni catalyst and its surface products, while $E_{(A/catalyst)}$ and $E_{(B/catalyst)}$ is the total energy of the surface substrate. Minus ΔH stands for exothermic reaction, while the positive ΔH stands for endothermic reaction.

Activation energy (E_a) is calculated according to the following formula:

$$E_a=E_{TS/catalyst}-E_{A+B/catalyst}$$

Therein, $E_{TS/catalyst}$ and $E_{A+B/catalyst}$ are the total energy of catalyst surface transition state and the total energy of catalyst and the reactants in co-adsorption respectively.

3. Results and Discussions

3.1 Energy changes of CH_4 dehydrogenation process

According to previous research, there are generally four elementary reactions in methane dehydrogenation process on Ni catalyst, and they are listed as follows:

$CH_4 + * \rightarrow CH_3\cdot + H^*$ (step 1)

$CH_3\cdot + * \rightarrow CH_2\cdot + H^*$ (step 2)

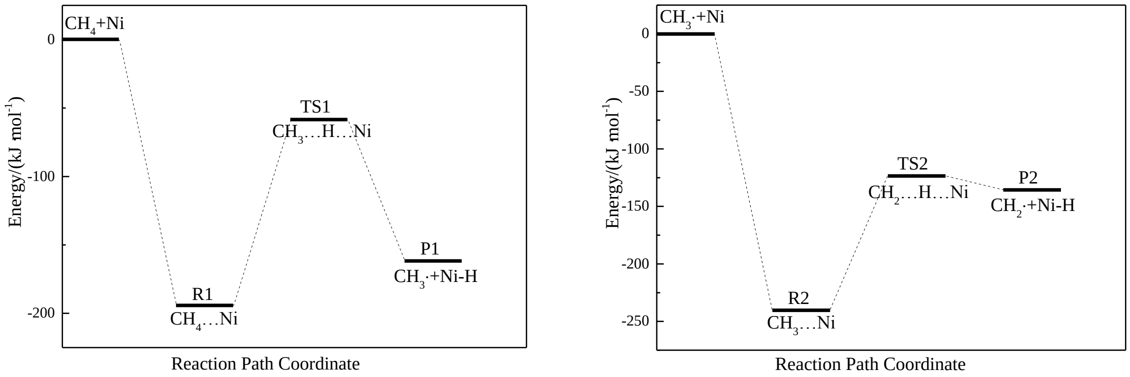
$CH_2\cdot + * \rightarrow CH\cdot + H^*$ (step 3)

$CH\cdot + * \rightarrow C\cdot + H^*$ (step 4)

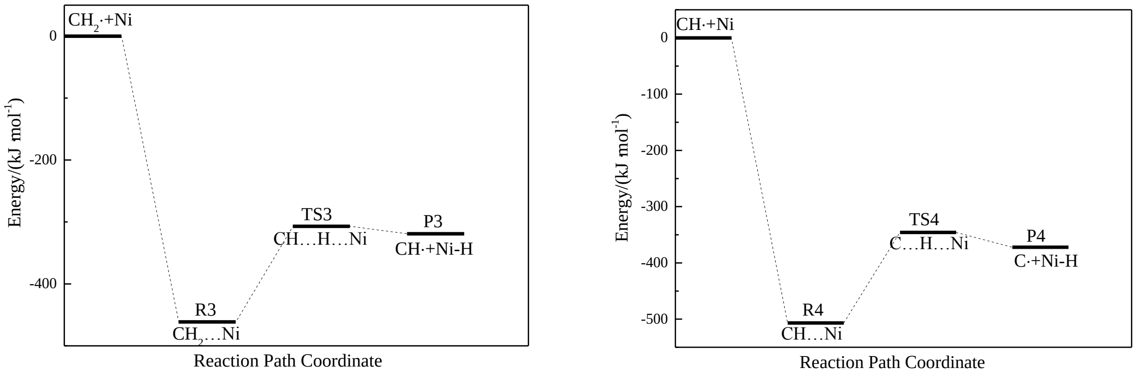
* stands for activated state.

By systematically calculating reaction enthalpy change (ΔH), energy barrier(E_a), and transition state (TS) structures of gradual CH_4 dehydrogenation reaction's elementary steps, the mechanism of CH_4 dehydrogenation process is further explored, and the results are shown in Figure 3-1.

The reaction of CH_4 dehydrogenation forming CH_3+H^* requires the system to cross 135.755 kJ·mol^{-1} energy barrier. The reaction is an endothermic process, and enthalpy is 32.451kJ·mol^{-1}. The higher reaction energy barrier shows that CH_4 dehydrogenation process is not supported by the kinetics. The process of $CH_3\cdot$dehydrogenation from $CH_3\cdot$to CH_2+H^* is an endothermic reaction which absorbs more heat than CH_4 dehydrogenation process, and the corresponding heat of is 104.600kJ·mol^{-1}. At the same time, the reaction energy barrier in the process is 116.747kJ·mol^{-1}. It is worth mentioning that, according to data, the reaction heat from $CH_2\cdot$dehydrogenation process is the largest in the gradual CH_4 dehydrogenation, which is 142.402kJ·mol^{-1}, and the reaction energy barrier is 154.473kJ·mol^{-1}. In the four elementary reactions, the $CH\cdot$dehydrogenation process from $CH\cdot$to $C+H^*$has the biggest reaction activation energy is the largest, and it is seen as a rate-determining step, which needs to overcome the energy barrier of 160.937kJ·mol^{-1} and with a 134.578kJ·mol^{-1} enthalpy change. Under Ni catalyst system, the high energy barrier and strong endothermic nature of $CH\cdot$dehydrogenation shows that the reaction is not likely to happen in thermodynamics and kinetics. It is thus inferred that $CH\cdot$free radicals may be enriched on the surface of Ni in great quantities. In addition, the fourth step reaction of methane dehydrogenation judged according to the activation energy is $CH\cdot+*\rightarrow C\cdot+H^*$ process, and it is the rate-determining step. In the methane disaggregation process, $CH\cdot$ disaggregation has the highest energy barrier, which also suggests that $CH\cdot$dehydrogenation is the rate-determining step of the whole CH_4 disaggregation process. This result is consistent with the previous research results by Ricardez-Sandoval et al[17].



$CH_4 + * \rightarrow CH_3 \cdot + H^*$ $CH_3 \cdot + * \rightarrow CH_2 \cdot + H^*$



$CH_2 \cdot + * \rightarrow CH \cdot + H^*$ $CH \cdot + * \rightarrow C \cdot + H^*$

Fig. -1 the energy profits of the dehydrogenation process from CH4 to C ·

3.2 Structural analysis of CH4 dehydrogenation process

Figure 3-2 shows the structural change of the gradual methane dehydrogenation process. At the beginning of $CH_4 + * \rightarrow CH_3 + H^*$, the C-H bond length is 1.100 Å and the distance from C to Ni is 3.924Å. At this point, absorbed by Ni, CH_4 is in a stable chemical adsorbed state, and according to frequency analysis, there is no imaginary frequency. In the activated C-H bond, H atom approaches Ni atom gradually to form TS1; according to the frequency analysis, TS1 has one and only one imaginary frequency, and its vibration direction is the same as the direction of the reaction, and TS1 is thus judged as reaction transition state. In the transition state TS1, the bond lengths of C-H bonds which do not participate in the reaction are1.101Å, 1.101Å and 1.106Å respectively, and the distance between H atoms (H_a) participating in the reaction and C atoms is 1.789 Å and the distance between H atoms (H_a) and Ni is 2.077Å; at the same time, C-H bonds are being fractured. Eventually, CH_3 and H-Ni are formed, and the frequency analysis results show that there is no imaginary frequency; the distance between H atoms and Ni atoms is 1.572Å, and the distance between H atoms and C is 1.987Å.

The initial state of the second reaction of methane dehydrogenation $CH_3 \cdot + * \rightarrow CH_2 \cdot + H^*$ is CH_3 ·stable chemical adsorbed state, and according to frequency analysis, there is no imaginary frequency. The bond length of the three C-H bonds is 1.105 Å each, and the distance between C atom and Ni atom is 1.915 Å; and then through the transition state TS2, products CH_2 · and H-Ni are finally formed. According to frequency analysis, TS2 structure has one and only one imaginary frequency, and its vibration direction is the same as the direction of the reaction, and therefore, TS2 is thus judged as reaction transition state. In the structure of transition state TS2, the bond lengths of C-H bonds which are not involved in the reaction change into 1.104Å and 1.101Å. The distance between H_a participating in the reaction and C is 1.865Å, and the bond length of the H-Ni bond is 1.603Å. The frequency analysis results of the products in the final state show that there is no imaginary frequency and the bond lengths of C-H bond in the final products CH_2 are 1.103Å and 1.104Å each, and that of H-Ni bond is 1.503Å.

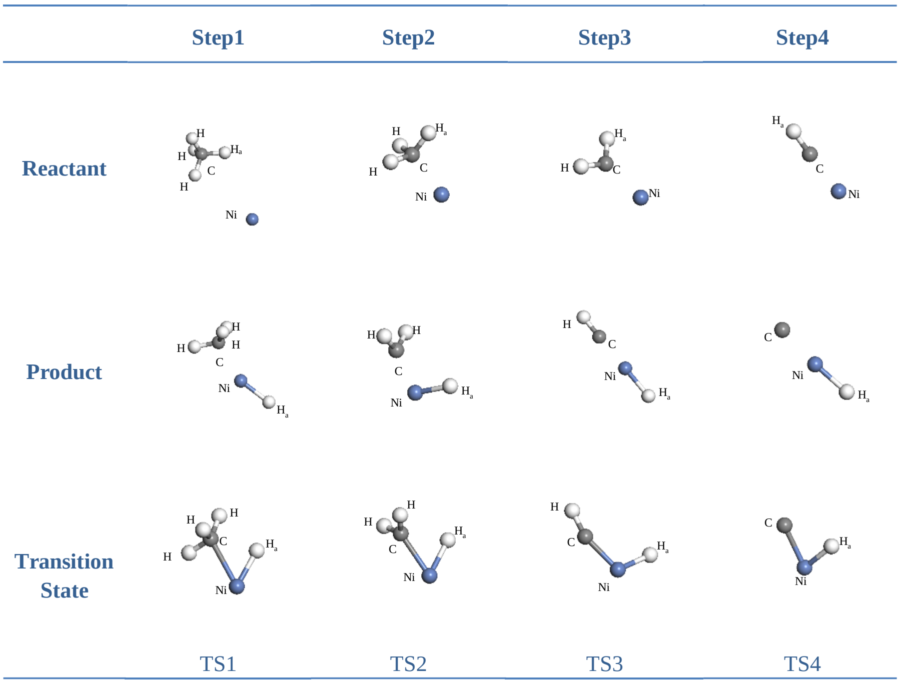


Fig. 3-2 Geometric structures of the reactant, transition state (TS), and product of the four steps of CH4 dehydrogenation on Ni catalyst Blue (Ni), gray (C), and white (H)

The initial state of $CH_2\cdot$dehydrogenation is $CH_2\cdot$stable chemical adsorbed state, and according to frequency analysis, there is no imaginary frequency. The distance between two C-H bonds are both 1.102 Å, and the distance between C atom and Ni atom is 1.832Å. According to frequency analysis, TS3 structure has one and only one imaginary frequency, and its vibration direction is the same as the direction of the reaction, and therefore, TS3 is thus judged as reaction transition state. In the structure of transition state TS3, the bond lengths of C-H bonds which are not involved in the reaction is 1.111Å, and the distance between H_a participating in the reaction and C is 1.865Å, and the bond length of the H-Ni bond is 1.603Å. The distance between H_a participating in the reaction and C is2.609Å, and the distance between H_a and catalyst Ni atom is 1.511Å. Later, H_a continues to go away from C atom, and the final products CH and H-Ni are formed; the frequency analysis results show that there is no imaginary frequency and the bond lengths of C-H bond is 1.105Å, and that of H-Ni is 1.576Å.

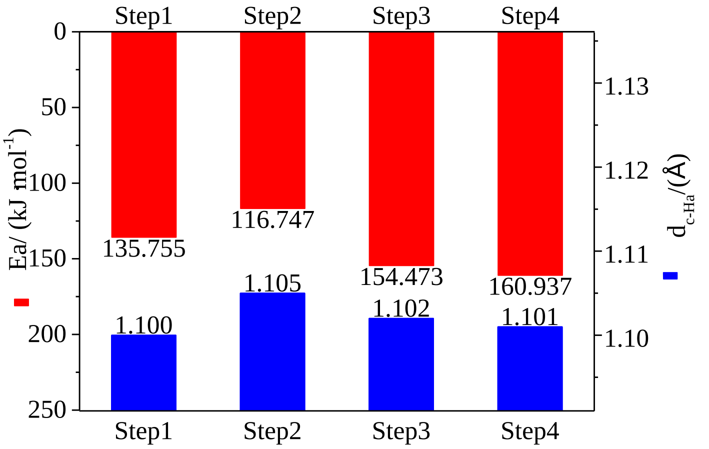


Fig. 3-3 the relationship between the C-Ha bond length of initial state and the activation energy of elementary reaction

The initial state of $CH\cdot$dehydrogenation $CH\cdot + * \rightarrow C\cdot + H^*$ is stable chemical adsorbed state, and according to frequency analysis, there is no imaginary frequency. The bond length of C-H bond is

1.101Å and the distance between C atom and Ni is 1.786Å. According to frequency analysis, TS4 structure has one and only one imaginary frequency, and its vibration direction is the same as the direction of the reaction, and therefore, TS4 is thus judged as reaction transition state. In the transition state TS4, the distance between C and H_a is 2.000Å, and that between H_a and Ni is 1.508Å. The final products C and H-Ni are formed; the frequency analysis results show that there is no imaginary frequency and the bond length of H-Ni bond is 1.580Å.

Figure 3-3 shows the relationship between the C-Ha bond length of initial state (that is CH_x species under the chemical adsorbed state) and the activation energy of elementary reaction. By contrast, it is found that the longer the bond length of C-H bond under the initial state is pulled, the smaller the reaction energy barrier becomes, which proves that Ni activation is stronger.

3.3 Charges population analysis of CH_4 dehydrogenation process

In order to understand deeply the reaction mechanism and the electronic structures of CH_x (x=0~4) and H · in which Ni atom participates, the paper makes systematic calculations on the corresponding Mulliken's charge population and molecular orbital.

As shown in Table 3-1, according to Mulliken charges population analysis, in the free CH_4 molecules, the quantities of electric charge of C atom and four H atoms are respectively -0.676 and 0.169, 0.169, 0.169, 0.169; C atom is negatively charged and H atoms are positively charged. When CH_4 is in a stable absorbed state, the quantities of C atom and four H atoms are respectively -0.845 and 0.211, 0.209, 0.205, 0.209, and the electric charge of the corresponding Ni atom is 0.016. At this point, C atom is still with negative charge, but the charge becomes obviously more; H atoms are positively charged, but their electric charge also slightly increases respectively, and there is an obvious difference among the four H atoms, Ni atom is correspondingly with positive charge. It shows that it is through electron-donating that Ni atom catalyzes the dehydrogenation reaction of CH_4 and the polarity of C-H bond in the CH_4 molecule in the chemical adsorbed state increases.

In the absence of external factors, in methyl radical (CH_3 ·), the quantities of electric charge of C atom and three H atoms are -0.633, 0.178, 0.178, 0.178 respectively. Considering the catalyst's chemical adsorption of CH_3 ; the quantities of electric charge of C atom and three H atoms are -0.828, 0.207, 0.207, 0.207, and meanwhile the charge of Ni atom is 0.208. The same as CH_4 molecule's chemical adsorption state, there is an increase in both negative charges carried by C atoms and positive charges carried by H atoms in CH_3 ; Ni atoms under the methyl chemical adsorption state system is also positively charged. Different from CH_4 chemical adsorption's charges population, the three H atoms in their chemical adsorption state carry the same quantity of positive charge, so it can be concluded that in the aspect of charges population, the three H atoms of the methyl have the same difficulty degree of dehydrogenation.

In the absence of external factors, the charges population of methylene radical (CH_2 ·) is: the quantities of electric charge of C atom and two H atoms are -0.372, 0.186, 0.186 respectively. Under the state of chemical adsorption, the charges population of methylene radical (CH_2 ·) is: the quantities of electric charge of C atom and two H atoms are -0.660, 0.210, 0.210 respectively, and meanwhile the charge of Ni atom is 0.240. This is similar to the changes before and after the chemical adsorption of CH_3 ; that is, there is an increase in both negative charges carried by C atoms and positive charges carried by the two H atoms; and the two H atoms' charge increase before and after chemical adsorption state is the same. In other words, the two H atoms in CH_2 are equivalent in the charges population.

Without the influence of external factors, the quantities of electric charge of C atom and H atom in methylidyne (CH ·) are -0.149 and 0.149 respectively. Under the state of chemical adsorption, the quantities of electric charge of C atom and H atom are -0.447 and 0.213 respectively, and the charge population of Ni atom, the corresponding adsorbent, is 0.234. After the chemical adsorption, in methylidyne (CH ·), negative charges carried by C atom increases significantly and positive charges carried by H atom also have a larger growth.

It can be found from the above, being absorbed by Ni catalyst, CH_x (x=1~4) has a new arrangement of charges population, and Ni catalyst plays a role of donating electrons when catalyzing the dehydrogenation of CH_4. The order of positive charges carried by Ni in the following systems is: CH-Ni > CH_2-Ni > CH_3-Ni > CH_4-Ni. The greater positive charges the Ni catalyst carries, the greater the amount of charge transfer.

Table -1 Mulliken charges population analysis of CH4 dehydrogenation process

Group	Atom	Mulliken charges population	Group	Atom	Mulliken charges population
CH_4	C	-0.676	CH_4-Ni	C	-0.845
	H(1)	0.169		H(1)	0.211
	H(2)	0.169		H(2)	0.209
	H(3)	0.169		H(3)	0.205
	H(4)	0.169		H(4)	0.204
				Ni	0.016
$CH_3\cdot$	C	-0.633	CH_3-Ni	C	-0.828
	H(1)	0.178		H(1)	0.207
	H(2)	0.178		H(2)	0.207
	H(3)	0.178		H(3)	0.207
				Ni	0.208
$CH_2\cdot$	C	-0.378	CH_2-Ni	C	-0.660
	H(1)	0.186		H(1)	0.210
	H(2)	0.186		H(2)	0.210
				Ni	0.240
$CH\cdot$	C	-0.149	CH-Ni	C	-0.447
	H	0.149		H	0.213
				Ni	0.234

3.4 Analysis of orbital properties in CH4 dehydrogenation process

Methane is the simplest alkane, the electron configuration of whose molecules is similar to inert gas; there are neither double bonds, triple bonds in methane's molecules, nor lone pairs, and it has a regular tetrahedron configuration of great symmetry. This kind of structure makes methane stable, and therefore, any conversion is conducted only after methane's molecules with great thermodynamic stability are activated. Therefore methane molecular activation has always been the most challenging subject in the field of catalysis.

In structural chemistry, the application of frontier molecular orbital (FMO) theory has successfully explained a series of chemical reactions. From the perspective of FMO theory, there are two ways to activate molecules: one is to remove electrons from bonding orbital, which reduces the electron cloud density of, so that chemical bonding loosened, weakened, and then fractured; the second way is to fill electrons in the antibonding orbital to offset the bonding effect, which can also make the chemical bonding loosened, weakened, and even fractured. Table 3-2 shows the electron configuration of Ni atom in the process of CH_4 dehydrogenation; Figure 3-4 presents molecular orbital's combination and change rules under the interaction between Ni atoms and CH_x (x=0~4), H. So to speak, Ni catalyst only play its catalytic activity when it forms the delocalized molecular orbital after it goes through 3d, 4s and 4p orbital hybridization. Through calculation, the configuration of Ni valence electron is 4s(1.11)3d(8.89)4p(0). In 4s(1.11)3d(8.89)4p(0) electron configuration state, there is a single electron under the condition of low spin having good coupling with s orbital and d orbital, which greatly avoids the big steric hindrance between CH_x·(x=0~4) species and Ni atom' s s orbital, d orbital and p orbital.

The highest occupied orbital (HOMO) of CH_4 is three equivalent σ bonding orbital, the lowest unoccupied molecular orbital (LUMO) is a σ^* antibonding orbital. First, an electron on C atoms' 2s orbital transited to four sp^3 hybridization orbitals formed by 2p orbital, and the energy level of the four sp^3 hybridization orbitals are not completely the same: the energy level of the original three 2p orbitals are reduced and form three sp^3 hybridization orbitals with slightly high level; and the energy level of the original 2s orbital goes up and form sp^3 hybridization orbitals with slightly low level. Then, electrons on the four H atoms' 1s orbital form bonds with four sp^3 hybridization orbitals, forming a σ bonding orbital with three slightly high level and a slightly low level. Meanwhile, the corresponding empty antibonding orbital σ^** is formed. The energy level of the bonding molecular orbital is reduced, and the energy level of the antibonding molecular orbital is increased. When Ni catalyzes dehydrogenation of CH_4, Ni valence electron configuration is 3d(8.681)4s(1.315)4p(0.007). It can be seen from the configuration that it is mixed from the electron configuration of 3d(10) and 4s(1.11)3d(8.89)4p(0). Effect of catalyst probably originates from the interaction between an empty antibonding orbital σ^* and Ni's 4 p orbital. From the angle of energy level, the energy levels of the two frontier orbital interacting are close (within 6eV), and their symmetries are identical. Judged form the electronegativity, electron transfer direction is from the electrons on 4p orbital formed through Ni atomic orbital hybridization to CH_4 LUMO (σ^*) (electronegativity value: Ni-1.9, C-2.5, H-2.1), and the results and Mulliken charge analysis results support each other. Electrons transfer from Ni atoms to CH_4 to LUMO (σ^*), thus activating C-H bonds.

C atoms in CH_3 ·first have a sp^2 hybridization, an electron after excitation reaches from 2s orbital to 2p orbital, and with another 2p orbital and 2s orbital, they form three sp^2 hybridization orbitals; the three sp^2 hybridization orbitals have a single electron each, and the energy level of two orbitals is relatively high, the rest one is relatively low. The three single electrons form three σ bonding orbitals with three H atoms respectively on 1s orbital, and accordingly forming three antibonding orbitals σ^*; the energy level of the bonding orbital is reduced while the energy level of antibonding orbital rises. CH_3·'s HOMO is a $2p_z$ orbital, and there is only one single electron which is not hybridized or forms bonding. HOMO' is the bonding orbital formed by electrons on H's 1s orbital and electrons on 2p orbital through C hybridization, and LUMO is the corresponding antibonding orbital σ^*. When Ni catalyzes dehydrogenation of CH_3 ; valence electron configuration is 3d(9.247)4s(1.609)4p(0.144). After hybridization, electrons on Ni atom's d_{xz} orbital and d_{yz} orbital will interact with CH_3·'s HOMO', and then activate the C-H bond, and electrons on 4p orbital will interact with CH_3·'s HOMO. From the angle of energy level, the energy levels of the two frontier orbital interacting are close (within 6eV), and their symmetries are identical.

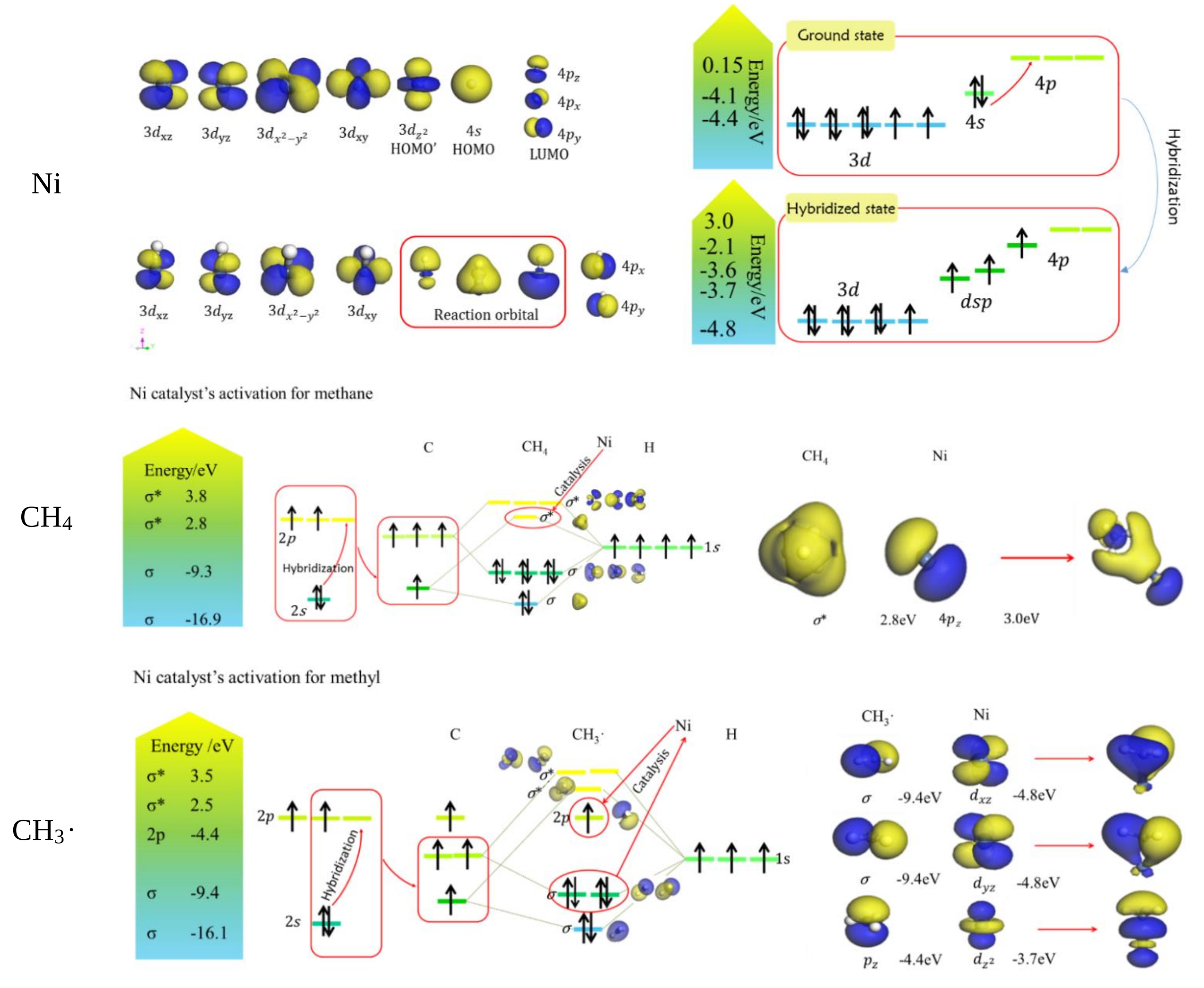
C atoms in CH_2 · go through sp^2 hybridization and form three sp^2 hybridization orbitals. One hybridization orbital with relatively high energy level and one with relatively low energy level form bondings with H atoms' 1s orbital respectively. Accordingly, bonding orbital σ and antibonding orbital σ^* are formed. CH_2· 's HOMO is 2p orbital where C atoms do not participate in hybridization, HOMO' is sp^2 orbital with the relatively high energy level after the hybridization of C atoms, and LUMO' is the antibonding orbital σ^* formed by hybridization orbital with relatively high energy level and H atoms' 1s orbital. When Ni catalyzes dehydrogenation of CH_2, valence electron configuration is 3d(8.899)4s(0.877)4p(0.224). After hybridization, electrons on Ni atom's d_{z2} orbital and d_{yz} orbital will interact with CH_2·'s HOMO and HOMO's single electron, and the electron transfer will make C with more negative charges and strengthen the C's attraction of H atoms which are positively charged, which makes the C-H bond more stable, and this is consistent with the relatively high activation energy of CH_2 ·dehydrogenation.

C atoms in CH ·does not have hybridization, HOMO orbitals are two 2p orbitals of C atoms which are unbonding, HOMO' orbital is the bonding orbital σ formed by electrons on H's 1s orbital and electrons on C's 2p orbital, and LUMO is the corresponding antibonding orbital σ^*. When Ni catalyzes dehydrogenation of CH, valence electron configuration is 3d(8.810)4s(0.854)4p(0.336). After hybridization, electrons on Ni atom's d_{xz} orbital and d_{yz} orbital will interact with the electrons of CH· 's HOMO, which does not weaken the electron transfer of C-H bond; the existing electron transfer will make C atoms with more negative charges, and strengthen the C's attraction of H atoms which are positively charged, which makes the C-H bond more stable, and this is consistent with the highest activation energy of CH ·dehydrogenation.

In conclusion, in the processes of Ni catalyzes methylene and methyne dehydrogenation, its interaction with C-H bond's bonding orbital and antibonding orbital is relatively weak, which cannot effectively activate C-H bond fracture; on the contrary, Ni's interaction with the single electron on C atoms' 2p orbital and empty orbital is relatively strong, and this will only increase C atoms' negative charges, which will further increase the attraction [18]to negatively charged H atoms. Therefore, the activation energy of methane and methyl dehydrogenation is relatively small, and the activation energy of methylene and methyne dehydrogenation is relatively big; because the stability of methane is higher than that of methyl, the activation energy of methane dehydrogenation is greater than that of methyl dehydrogenation.

Table-2 Electron configuration of Ni atoms in different states

State	Electron configuration
Ni(Ground state)	[core]4s(2)3d(8)
Ni(Hybridized state)	[core]4s(1.11)3d(8.89)
Ni-H	[core]4s(1.594)3d(9.257)4p(0.149)



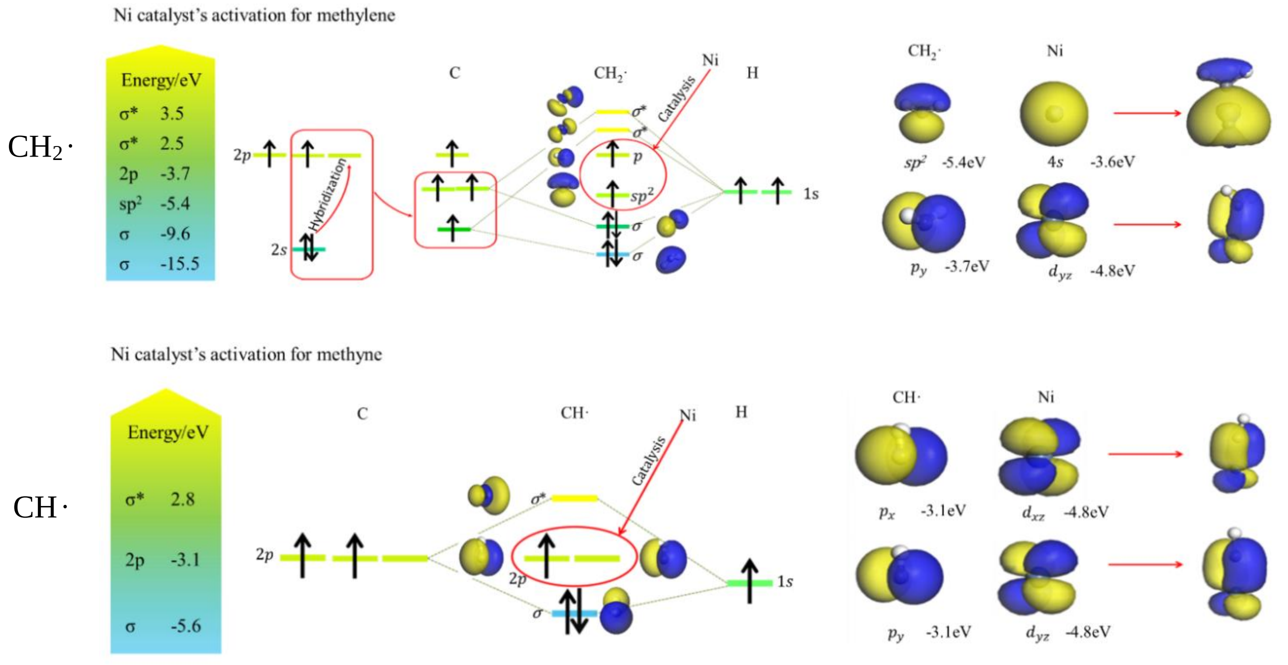


Fig. -4 Frontier molecular orbitals for CH4 dehydrogenation process calculated by DFT Yellow (+) for alpha spin and blue (-) for beta spin

4. Conclusion

Based on ab initio calculation method and the quantum mechanics of first principles, the energy, structural change, charges population and orbital interaction of CH_4 continuous dehydrogenation process are calculated in this paper respectively. Results show that in four elementary reactions of CH_4 dehydrogenation, the activation energy maximization of CH · dehydrogenation on Ni is a rate-determining step in the whole process of dehydrogenation, and the activation energy is 160.937kJ·mol^{-1}. It is inferred that CH · free radicals may be enriched on the surface of Ni in great quantities. By comparing the relationship between the bond length of reactants CH_x (x=1~4) under the chemical adsorbed state in the gradual methane dehydrogenation process and the activation energy accordingly, it is found that the longer the bond length of C-H bond is pulled, the smaller the reaction energy barrier becomes. Through the analysis of reactant molecules and product molecules in reaction process, Mulliken founds that being absorbed by Ni catalyst, CH_x (x=1~4) has a new arrangement of charges population, and Ni catalyst plays a role of donating electrons when catalyzing the dehydrogenation of CH_4. The order of positive charges carried by Ni in the following systems is: CH-Ni > CH_2-Ni > CH_3-Ni > CH_4-Ni. The greater positive charges the Ni catalyst carries, the greater the amount of charge transfer. Results of the orbital analysis shows that in the processes of Ni catalyzes methylene and methyne dehydrogenation, its interaction with C-H bond's bonding orbital and antibonding orbital is relatively weak, which cannot effectively activate C-H bond fracture; on the contrary, Ni's interaction with the single electron on C atoms' 2p orbital and empty orbital is relatively strong, and this will only increase C atoms' negative charges, which will further increase the attraction[18] to negatively charged H atoms. Therefore, the activation energy of methane and methyl dehydrogenation is relatively small, and the activation energy of methylene and methyne dehydrogenation is relatively big; because the stability of methane is higher than that of methyl, the activation energy of methane dehydrogenation is greater than that of methyl dehydrogenation.

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