A New Reforming Reaction Mechanism of Carbon Dioxide with Methane on Nano Scale Nickel catalyst

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Abstract. The reforming mechanism of CO_2-CH_4 on Nano scale Ni metal catalyst was investigated using the B3LYP density functional method and MP2/Lanl2dz method. It was found that the reaction include thirteen steps and the activation energy of each step was 44.7175, 200.4707, 171.0781, 307.2596, 124.5252, 330.7904, 593.9056, 177.5526, 226.6793, 277.789 2, 394.5525,399.5340 and 105.4115 kJ·mol^{-1}. The rate determining step was the fourth step. The enthalpy value of each step was 31.6136, 106.7138,－104.2589, 79.9641, 93.5573,174.6 121, 259.6409, －141.9192,－439.9338, －265.4756,－208.3245, 131.6561 and －86.1765 kJ·mol^{-1}.

1. Introduction

The carbon dioxide reforming of methane had received a large number of experimental studies [1-3], because it could not only greatly improve the utilization of natural gas,but also maybe reduce carbon dioxide's emission,and it was conducive to energy saving.Because of catalyst coke,this reaction had not been industrialized[4], and CO_2-CH_4 reforming reaction mechanism had not reached unity for a long time[5].

Adequate experiments[6-7] had showed that Nano scale Ni metal catalyst was the best catalyst for CO_2-CH_4 reforming reaction. Vannice[8] had proposed mechanism of surface oxygen in the scientific community that had reached unanimous approval, the main process was shown in the Figure 1.

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$$CH_4 + * \longrightarrow CH_3* + H\cdot$$
$$CO_2 + H\cdot \longrightarrow CO + \cdot OH$$
$$CH_4 + O* \longrightarrow CH_3* + \cdot OH$$
$$CH_3* + (3\text{-}x)* \longrightarrow CH_x* + (3\text{-}x)H*$$
$$CH_x* + O* \longrightarrow CO + xH*$$
$$CH_x* + CO_2 \longrightarrow 2CO + xH*$$
$$2H\cdot \longrightarrow H_2$$
$$2OH\cdot \longrightarrow H_2O + \cdot O\cdot$$

Fig.1 The reforming mechanism by surface oxygen (* was the central atom catalyst)

The key functional groups were –OH and [O] radical in this reforming mechanism,but it wasn't explained the existence of specific form of surface oxygen in this reaction system.The thermodynamic value of each step response was not clear,so we had chose theory research method to explore the thermodynamic value and which step was difficult or easy in the reaction.So far, the theoretical study of CO_2-CH_4 reforming reaction was not much[9].This mechanism of theoretical research was good help and guidance to further experiments.

2. Methods

All calculations were done by the Gaussian 03 program[10] in Computing workstations on the China Scientific Computing Grid(ScGrid). Geometry optimization had been carried out at the B3LYP/Lanl2dz level along with analytic vibrate frequency calculation in order to characterize the obtained structure as minimum or as transit states on the potential energy surface.In some previous studies[11], the theoretical level MP2/Lanl2dz appeared to be economical and successful in dealing with the reaction.The vibration analysis had showed that reactants, intermediates and the torque constant of products were positive value.It was certain that they were stably exist.The torque constant of the transition state product had one and only negative eigenvalue, which had demonstrated the resulting transition state was credible.

3. Results and Discussions

According to literature provided, the reforming mechanism in this reaction could be divided into 13 steps,the chemical reaction equation of each step was showed in detail by Figure 2. At the first step, the methane can absorbed on the surface of nickel metal, which can form the intermediate radical as CH_3Ni. It was so easy to dissociate hydrogen atom into radical as CH_2Ni , -CHNi and C-Ni. At the same time, the carbon dioxide molecule can combine the hydrogen free radical in order to produce many ·OH free radicals. The oxygen radical free radical can be produced through the collision of two ·OH free radicals.

In order to explore the microscopic mechanism of the reaction, we try to explore the process in the different intermediate free radicals. We found a lot of the react progress could not be taken directly, and the surface oxygen atom radical was prefer to the radicals as CH_2Ni and C-Ni, the NiO radical was prefer to the CH_2Ni and CH_4 radicals, and the CO_2 molecule can response with the CH_2Ni and C-Ni directly.

$$CH_4 + Ni \rightarrow CH_3Ni + \cdot H \quad (1)$$
$$CO_2 + H\cdot \rightarrow CO + \cdot OH \quad (2)$$
$$CO_2 + Ni \rightarrow NiO + CO \quad (3)$$
$$CH_4 + NiO \rightarrow CH_3Ni + \cdot OH \quad (4)$$
$$CH_3Ni \rightarrow CH_2Ni + \cdot H \quad (5\text{-}1)$$
$$CH_2Ni \rightarrow \text{-}CHNi + \cdot H \quad (5\text{-}2)$$
$$\text{-}CHNi \rightarrow C-Ni + \cdot H \quad (5\text{-}3)$$
$$CH_2Ni + NiO \rightarrow CO + 2HNi \quad (6)$$
$$CH_2Ni + \cdot O\cdot \rightarrow CO + HNi + \cdot H \quad (7)$$
$$C-Ni + \cdot O\cdot \rightarrow CO + Ni \quad (8)$$
$$CH_2Ni + CO_2 \rightarrow 2CO + HNi + \cdot H \quad (9)$$
$$C-Ni + CO_2 \rightarrow 2CO + Ni \quad (10)$$
$$2H\cdot \rightarrow H_2 \quad (11)$$
$$2\cdot OH \rightarrow H_2O + \cdot O\cdot \quad (12)$$

Fig.2 Each step of the CO_2-CH_4 reforming reaction

The beginning of the CO_2-CH_4 reforming reaction was methane's dehydrogenate over supported nickel as the catalyst.Ni could adsorb methane on the surface.Previous studies[6,7,12] had shown that it was very easy that methane took off one hydrogen atom,but it was difficult to take off more hydrogen atoms.Also CH_3Ni has high activity,free hydrogen atoms could be offend CO_2 to generate OH,but nickel adsorbed CO_2 to generate surface oxygen is easier,and surface oxygen could activate more intermediate.

Formula 5-1,5-2,5-3 had indicated the process of gradual intermediate dehydrogenate, Further dehydrogenate product could be a good follow-up reaction with the surface oxygen by formula 6,7,8.It was found that the surface oxygen could be active to react with the dehydrogenate products,CH_2Ni was the most active substance.The specific relationship of each material was shown in Figure 3.

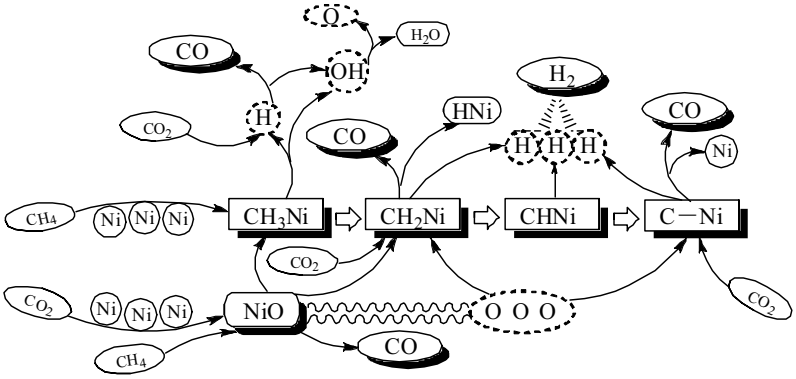
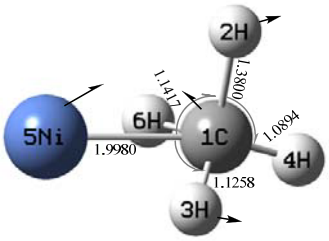


Fig.3 Each relationship along each substance step of CO_2-CH_4 reforming reaction

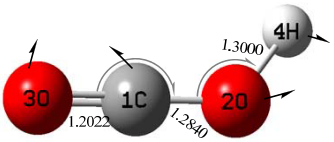
4. Analysis of Transition State

It was found that many transition states in most steps by full optimization calculation.It was clearly that the orientation of the key atomic vibrations and the movement of transition state, which was further proof of the authenticity of the transition state. The virtual vibration mode of transition state in each step had been shown in Figure 4, so the TS1,TS2,TS3,TS4,TS6, TS7,TS9,TS10 was on behalf of the transition states in the many steps respectively.



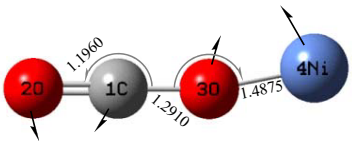
A[5Ni-1C-2H]=91.3895
A[5Ni-1C-3H]=68.3735
A[2H-1C-4H]=107.2104

TS1



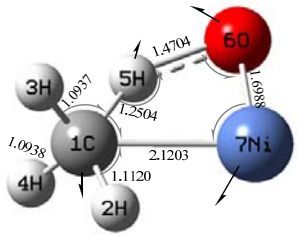
A[3O-1C-2O]=179.9721
A[1C-2O-4H]=127.2810

TS2



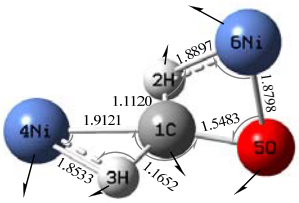
A[2O-1C-3O]=179.9800
A[1C-3O-4Ni]=165.2771

TS3



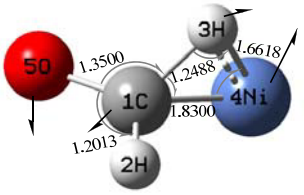
A[3H-1C-5H]=100.9289 A[1C-5H-6O]=147.3536
A[2H-1C-7Ni]=72.4150 A[5H-6O-7Ni]=68.9983
A[5H-1C-7Ni]=58.1011 A[6O-7Ni-1C]=85.5464
D[1C-5H-6O-7Ni]=0.3374 D[3H-1C-7Ni-6O]=-81.5133
D[1C-7Ni-6O-5H]=-0.10766 D[3H-1C-5H-6O]=122.6142

TS4



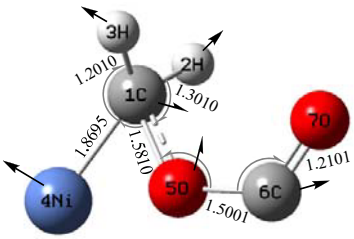
A[3H-1C-4Ni]=62.8047 A[1C-3H-4Ni]=80.3127
A[3H-1C-5O]=115.5110 A[5O-6Ni-2H]=57.6665
A[1C-5O-6Ni]=75.7937 A[1C-2H-6Ni]=69.1840
D[2H-1C-5O-6Ni]=75.1223
D[5O-1C-3H-4Ni]=-164.8644

TS6



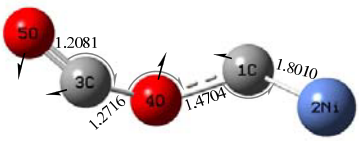
A[3H-1C-4Ni]=61.9826
A[5O-1C-2H]=119.6201
A[5O-1C-3H]=117.4225
A[1C-3H-4Ni]=124.2220

TS7



A[5O-6C-7O]=117.7771 A[3H-1C-4Ni]=123.2278
A[1C-5O-6C]=124.3057 A[4Ni-1C-5O]=68.0580
A[2H-1C-5O]=112.3420 D[1C-5O-6C-7O]=-1.2690
D[4Ni-1C-5O-6C]=176.2286

TS9



A[4O-3C-5O]=146.5230
A[3C-4O-1C]=143.7361
A[4O-1C-2Ni]=120.2463
D[3C-4O-1C-2Ni]=96.1532

TS10

Fig.4 Many imaginary vibration mode of each step in the CO_2-CH_4 reforming reaction

We found the nickel metal atom could adsorb the methane molecule in TS1, and the methane molecule will lose one hydrogen atom in order to form the CH_3Ni active radial. The

carbon dioxide molecule cloud change into the carbon monoxide molecule through the hydrogen active radial in TS2 or nickel metal in TS3 respectively. As shown in the TS4 and TS6, we found the NiO active radial could catalyze the methane or CH_2=Ni radial, and the two OH active radial will condensate into the O active radial. We also found the CH_2=Ni radial is not stable which can be catalyzed easily by the O active radial as shown in TS7 or CO_2 as shown in TS9. As shown in TS10, we also found the C-Ni radial can catalyze the carbon dioxide molecule easily. All of transient states is credible because our calculate method is reasonable and many experiment results [12]could be agree with our calculate results.

5. Analysis of Thermodynamic Energy Data

On the basis of the optimized geometry calculation by B3LYP/Lanl2dz, many perturbation methods were used in order to calculate the reaction's thermodynamic data.It was found that MP2/Lanl2dz should be the best calculation method.The calculated data by MP2/Lanl2dz was shown in table 1.All of these conclusions were fully consistent with experimental data[13].

TABLE 1 THE THERMODYNAMIC DATA OF EACH STEP IN THECO_2-CH_4 REFORMING REACTION.(T=298.15K,P=100.00KPA)

Step	$\triangle_r E$ (kJ·mol^{-1})	$\triangle_r E^r$ (kJ·mol^{-1})	$\triangle_r H$ (kJ·mol^{-1})	Step	$\triangle_r E$ (kJ·mol^{-1})	$\triangle_r E^r$ (kJ·mol^{-1})	$\triangle_r H$ (kJ·mol^{-1})
（1）	44.7175	13.1039	31.6136	（6）	177.5526	319.4718	—
（2）	200.4707	93.7569	106.7138	（7）	226.6793	666.6131	—
（3）	171.0781	275.3370	—	（8）	277.7892	543.2648	—
（4）	307.2596	227.2955	79.9641	（9）	394.5525	186.2280	208.3245
（5-1）	124.5252	30.9679	93.5573	（10	399.5340	267.8779	131.6561
（5-2）	330.7904	156.1783	174.6121	（11	—	—	—
（5-3）	593.9056	334.3007	259.6049	（12	105.4115	191.5880	−86.1765

The Heat enthalpy and the activation energy for each step were calculated using MP2/Lanl2dz method (basis set) had explained that the most of the steps were endothermic,and a small amount of steps were exothermic.According to every step's activation energy data, The CH_2Ni or C—Ni were difficult to react with CO_2, but surface oxygen was easy to react with CH_2Ni or C—Ni. The rate determining step was the fourth step,because the activation energy was 307.2596 kJ·mol^{-1}. Small amount of water had been produced by step 12.It was no difference to the CO_2-CH_4 reforming reaction system,but a trace of surface oxygen could have a great role in promoting of the reforming progress.

6. Summary

Nano Scale Nickel metal as the catalyst in the CO_2-CH_4 reforming reaction system, the activation energy of each step was 44.7175,200.4707,171.0781,307.2596,124.5252,330.7904,593.9056, 177.5526, 226.6793, 277.7892,394.5525, 399.5340 and 105.4115kJ·mol^{-1}. The rate determining step was the fourth step. Enthalpy of every step was 31.6136,106.7138,−104.2589, 79.9641, 93.5573,

174.6121, 259.6409, －141.9192, －439.9338, －265.4756, －208.3245,131.6561 and －86.1765 kJ·mol^{-1}. Therefore, the surface oxygen radical had played a key role in the CO_2-CH_4 reforming reaction system.

7. Acknowledgment

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