

Study on Carbon - Oxygen Catalytic Combustion Mechanism based on Density Functional Theory

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ABSTRACT: Catalytic combustion is an important technique for utilization of fossil fuels, and the research on catalytic combustion mechanism could provide theoretical basis for the selection of catalyzer. In this paper, we adopt the Ni catalyst to promote the oxidation combustion reaction, and carry out study on carbon - oxygen catalytic combustion mechanism based on density functional theory. The result suggests that Ni catalyst could significantly improve the carbon - oxygen catalytic combustion performance.

Density Functional Theory Overview

Density functional theory (DFT) is an expression form of quantum theory, which is developed based on Thomas-Fermi theory in 1960s. The wave function is seen as the basic physical system in traditional quantum theory, while density functional theory describes the physical properties of the ground state of the system by particle density, that is, the nature of the system is uniquely identified by its electron density distribution(ρ).

Like Hartree-Fock method, DFT also introduce three approximations: Born-Oppenheimer approximation, adiabatic approximation and single-electron approximation. Adiabatic approximation separates the motion of the nucleus from the motion of the electron; Hartree-Fock approximation could simplify the multi- electronic problem to a single - electronic problem. DFT provides the theoretical basis for solving the problem, as it considers the exchange energy and the correlation energy, and adopts a variety of methods to reduce the error. As for Relativistic effect, DFT also makes some amendments, so that describe the multi-electron system more accurately.

The basic idea of DFT is to use the particle density function to describe the physical ground state atoms, molecules and solids properties. However, the theoretical basis was not really determined until Hohenberg-Kohn first and second theorems were proposed. Subsequently, Kohn and Sham's job made DFT a feasible theoretical method.

Hohenberg-Kohn first and second theorems have many forms of expression, but here briefly introduce the commonly-used one:

(1) Hohenberg-Kohn first theorem

For an N electronic system regardless of spin that is in the outer potential field $V(r)$, the outer potential field $V(r)$ is uniquely identified by particle density (ρ). This theorem shows that the ground state of the particle density in multi-electron system is corresponding to the external potential field. Meanwhile, it determines the number of electrons in the system, and then determines all properties of the system. This theorem lays a solid theoretical foundation for the DFT.

(2) Hohenberg-Kohn second theorem

In case that total number of particles remains unchanged, the obtained ground state energy is equal to the minimum value of the energy functional. If density functional representation of system

energy is known, we can derive the ground state density from the variational condition, so that get all the physical properties of the ground state of the system.

According to Hohenberg-Kohn theorem, the ground state energy and the ground state particle density function could be obtained by variations of density function by energy functional. To complete the single particle image, construct density functions with N single particle wavelet function $\varphi_i(r)$.

$$\rho(r) = \sum_{i=1}^N |\varphi_i(r)|^2 \quad (1)$$

Thus, variations of $\rho(r)$ could be replaced by variations of $\varphi_i(r)$, while lagrange multipliers replaced by E_i . So we can obtain single-electron equation as follow:

$$\left\{ -\nabla^2 + V_{KS}[\rho(r)] \right\} \varphi_i(r) = E_i \varphi_i(r) \quad (2)$$

In the formula,

$$V_{KS}[\rho(r)] = V_{ext}(r) + V_c[\rho(r)] + V_{XC}[\rho(r)] = V_{ext}(r) + d r' \left| \frac{\rho(r')}{r-r'} \right| + \frac{\delta E_{XC}[\rho]}{\delta \rho} \quad (3)$$

The above three formulas constitute Kohn-Sham equation. The core of Kohn-Sham equation is to replace the particle Hamiltonian with interaction by the particle model without interaction, and then derive the single-electron equation. Similar to Hartree-Fock approximation, in DFT, single-electron Kohn-Sham equation derivation is strictly described.

Ni Catalytic Combustion Mechanism

Under the same conditions of combustion, adding of additives could obviously improve the combustion efficiency, e.g. H₂/Ar plasma pyrolysis testsimulates the rapid thermal decomposition of pulverized coal in raceway. Metal catalysts are recognized as the catalysts that have combustion catalyst effect. Ni catalyst plays a important role in reduce the ignition point of carbon-oxygen system, because it can effectively promote the interface reaction of carbon and oxygen, and it has high catalytic activity. However, it is easy to cause erosion of combustion equipment, meanwhile.

Composite catalyst is to mix two or more combustion supporting agents that have strengthened catalysis effect. In this study, we adopt the Ni-Al₂O₃ composite catalyst to promote the oxidation combustion reaction. The influence of nickel powder on carbon-oxygen catalytic combustion reaction is shown in Table 1.

Table 1. Influence of nickel powder on carbon-oxygen catalytic combustion reaction

No.	Component	Burn rate at different pressure (MPa) r/mm.s ⁻¹				n
		9	12	15	18	
1	Pure Al ₂ O ₃	9.374	10.77	11.98	13.53	0.53
2	2% Ni mixture	9.967	11.38	12.83	-	0.49
3	3% Ni mixture	9.969	11.48	12.96	13.32	0.42

From Table 1 we can see that, adding of nickel powder in catalyzer could significantly affect the combustion performance. When adding 3% Ni in the mixture, the burning rate pressure index would be decreased from 0.53 to 0.42, comparing to pure Al_2O_3 catalyzer.

The catalytic mechanism of Ni in Carbon – Oxygen reaction should focus on adsorption of oxygen molecules on Ni surface. Therefore, the first step in the catalytic process may be O_2 molecule stably adsorbing on the surface of Ni and generating activated oxygen species. Only in this way could Ni transfer the adsorbed oxygen species to the carbon surface. According to the above speculation, we divide the reaction process of Ni catalytic carbon – oxygen oxidation into three parts: ① generation of Ni surface active oxygen species; ② interaction between carbon and Ni surface active oxygen species; ③ reaction product removed from the Ni surface

(1) Generation of Ni surface active oxygen species

The configurations of O_2 molecule adsorbing on four different locations on the clean surface of Ni(111)-p(3×3×4) are shown as Figure 1, and the adsorption configuration parameters are shown in Table 2:

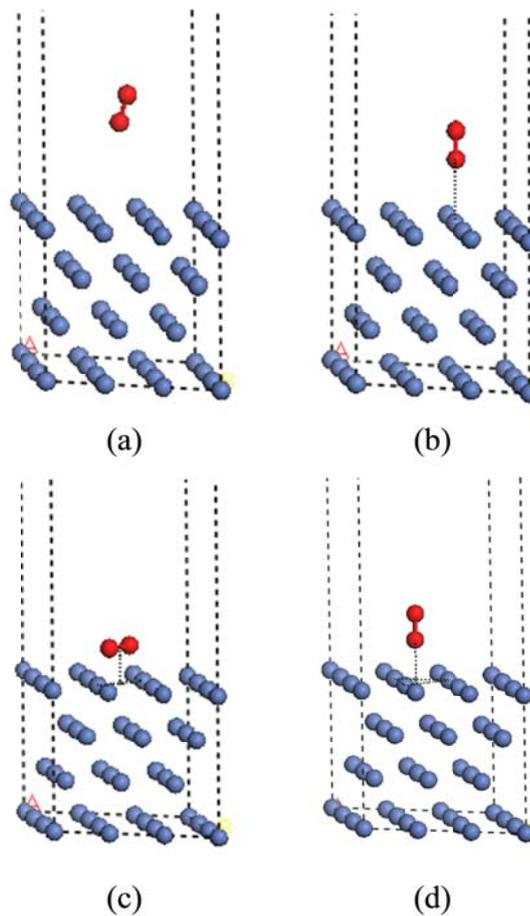


Figure 1. Physical adsorption configuration of O_2 on Ni(111), a) the O_2 adsorbed on the top of Ni atom, (b) the O_2 adsorbed on the top of Ni-Ni bridge, (d) the O_2 adsorbed on the top hollow

Table 2. Adsorption energy, distance between O_2 and surface atom, and distance between O-O bonds for O_2 adsorption on Ni(111) surface

Model	E_b/eV	d/A	d_{O-O}/A
Ni top	Unstable	2.518	1.242
Bridge	1.12	1.544	1.373
Hollow top	Unstable	2.251	1.236

From Table 2 we can see that, the adsorption configuration of O₂ on Ni-Ni_{bridge} is the most stable, which shows that the diffusion energy barrier of O₂ on this surface is relatively high, so it not easy to diffuse.

In order to analyze the bonding mechanism of O₂ adsorbed on the catalyst surface, we calculate the molecular density curve (DOS) of free O₂ and adsorbed O₂, as shown in Figure 2.

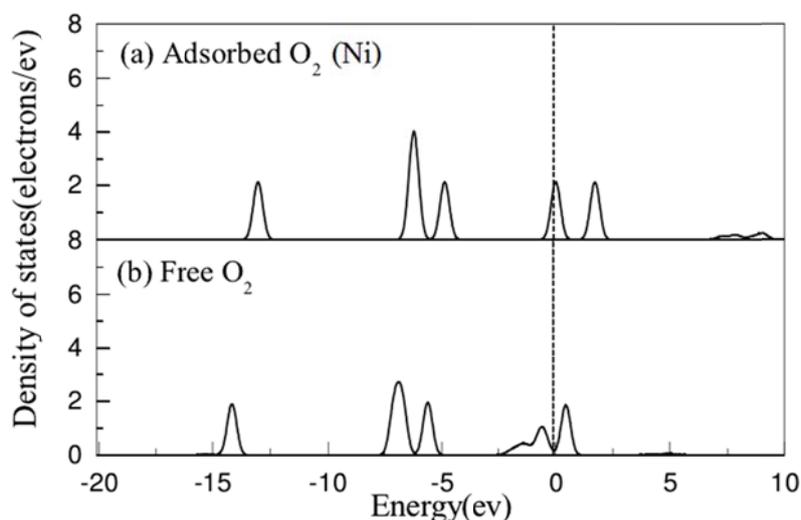
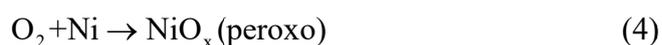


Figure 2. Molecular density curve of free O₂ and adsorbed O₂

The results shows that Ni(111) surface adsorption mode is exothermic reaction, and adsorption energy is large than energy in simple electronic reaction, so we can speculate that there is electron transfer between Ni and O₂. Oxygen molecules could stably adsorb in Ni-Ni bridges on the surface of Ni(111) and be activated, which provides reactive oxygen species for the subsequent reaction with carbon. This process can be expressed as:



(2) Interaction between carbon and Ni surface active oxygen species

The configurations before and after interaction between C₄ cluster and Ni(111) surface adsorbing oxygen molecule are shown in Figure 3.

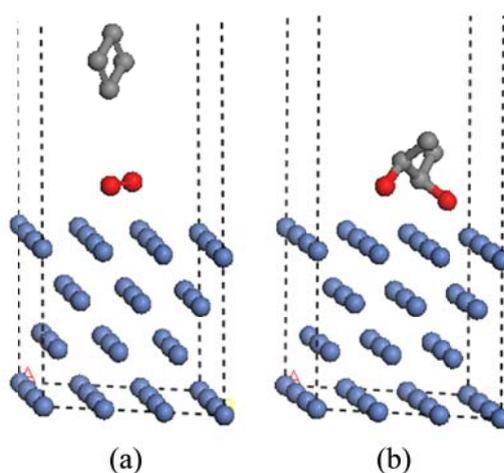
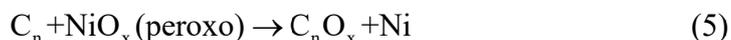


Figure 3. Adsorption configuration of a C₄ cluster on the O₂/Ni surface, (a) before adsorbed, (b) after adsorbed

By comparing the two configurations, after C₄ cluster adsorption, the structure appears distorted: two adjacent carbon atoms are bonded to the active oxygen atom, respectively; O-O bond length is stretched and broken off. Binding energy of this configuration is calculated to be 3.479 eV. It suggests that this process is a strong exothermic process, which can be spontaneous.

These results suggest that carbon clusters can be oxidized in O₂ / Ni surface, and the process can be expressed as:



(3) Reaction product desorbing from the Ni surface

In the above reaction configuration, C_nO_x or CO₂ will be removed from the Ni surface under certain conditions. The possible configurations of the reaction products desorption from the surface of Ni are shown in Figure 4.

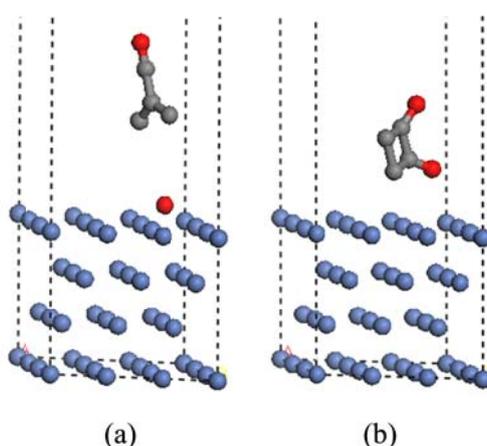


Figure 4. Possible configuration of product desorption from Ni surface, (a) Ni-O+C₄O, (b) Ni+C₄O₂

From the figure we can see that, the Ni surface configurations after desorption from C₄O and C₄O₂ has a great change. Calculating the energy configuration, it shows that the structural energy after adsorption is larger than that before desorption, so it is an endothermic process. Through transition state method, we calculate the configuration and energy barrier of transition states, as shown in Figure 5.

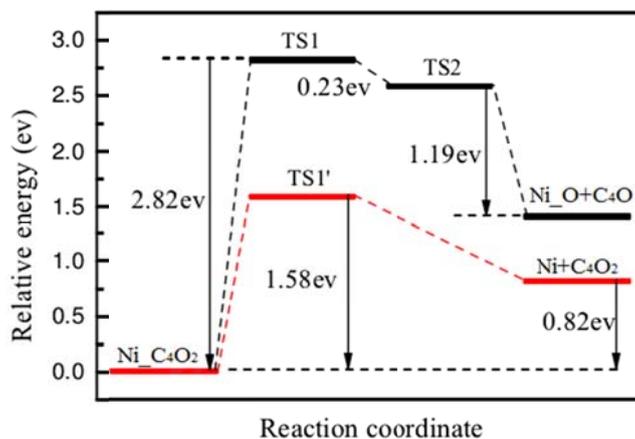


Figure 5. Potential energy diagram for different pathways of desorption of products on Ni surface

Figure 5 shows that it requires to absorb 1.400eV when C₄O desorbs from Ni-C₄O₂, and needs to cross the two energy barriers of 2.82eV and 2.59eV; while it just requires to absorb 0.82eV when desorbs as the form of C₄O₂, and the energy barrier is as low as 1.58eV.

Conclusion

Based on density functional theory, we have carried out systematic study on the process mechanism that the Ni-Al₂O₃ composite catalyzer promoting oxygen transfer in carbon-oxygen combustion reaction, and the results shows that: 1) adding of nickel powder in catalyzer could significantly affect the combustion performance; 2) the Ni-Ni bridge bond on surface of Ni(111) is the active site of the catalytic reaction, O₂ can adsorb and generate reactive oxygen species in these location; 3) C or CO is preferentially associated with the generation of reactive oxygen species, and the dissociation of the product is easy to occur. This study has explored the catalytic reaction path of Ni-Al₂O₃ composite catalyzer in carbon-oxygen system, and explained the oxygen transfer / release mechanism in catalytic combustion process.

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