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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ РЕАКЦИИ ГИДРОГЕНИЗАЦИИ МОНООКСИДА УГЛЕРОДА В МЕТАНОЛ НА ПОВЕРХНОСТИ СО (111)

Исследование реакции гидрогенизации монооксида углерода (CO) в метанол проведено с использованием теории функционала плотности и CI-NEB метода. Полученные результаты показывают, что монооксид углерод и водород легко адсорбируются на поверхности катализатора. Процессы адсорбции не проходят через переходные состояния. Предположен многостадийный механизм превращения CO в метанол. Рассчитаны значения энергии активации всех стадий.

Ключевые слова: гидрогенизация, монооксид углерод, метанол, адсорбция, механизм, теория функционала плотности, CI-NEB.

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THEORETICAL STUDY ON HYDROGENATION OF CARBON MONOXIDE TO METHANOL ON CO (111) SURFACE

The hydrogenation reaction of carbon monoxide (CO) to methanol (CH_3OH) on the Co (111) surface was investigated using density functional theory and a climbing image nudged elastic bond (CI-NEB) method. The results obtained indicate that carbon monoxide and hydrogen are easily adsorbed on the catalyst surface. The results also showed that the process of adsorbing CO and H_2 does not involve a transition state. A possible reaction pathway for the transformation of CO to CH_3OH was proposed. The activation energies of each step were also calculated.

Key words: hydrogenation, carbon monoxide, methanol, adsorption, mechanism, density functional theory, climbing image nudge elastic bond

INTRODUCTION

Catalytic conversion of syngas (CO + H_2) to liquid fuels is an important process addressing the energy and environmental issues of great interest. Previous studies have shown that metal catalysts such as cobalt, copper, iron and ruthenium are the most suitable for CO hydrogenation [1-3]. Cobalt is the catalyst which isused in industrial applications due to activity and cost. Although a number of theoretical and experimental works on the conversion of syngas on cobalt-based catalysts have been carried out, the study of mechanism of interaction between gaseous molecules with metal is quite rare.

The purpose of this work is to study the reaction mechanism of hydrogenation of carbon monoxide to methanol on the most common and stable surface of cobalt – Co(III).

MODELS AND COMPUTATIONAL METHODS

Based on the XRD analysis, Co(111) surface was chosen due to its stability and activity. The geometry optimization of structures Co(111) as well as H_2 and CO molecules were carried out using density functional theory in the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) gradient-corrected functional [4]. The double zeta basis plus polarization orbitals (DZP) is used for valence electrons, while core electrons are ‘frozen’ in their atomic state by using norm-conserving pseudo-potentials (NCP) in its fully nonlocal form [5]. The Brillouin-zone sampling is restricted to the Γ-point. All equilibrium structures are performed using Quasi Newton algorithm and the forces acting on the dynamic atoms all are smaller than 0.05 eV/Å.

In all calculations, the Co(III) surface and the isolated gas molecules CO and H_2 were firstly optimized to minimize their total energies. Each of these individual molecules was kept at different adsorption sites and the adsorption configurations were optimized to get the lowest energy stable structure.

The adsorption energy (E_{ads}) was defined as:

$$E_{ads} = E_{adsorbate\text{-}substrate} - (E_{adsorbate} + E_{substrate}) \quad (1)$$

The adsorption energy is an important parameter to evaluate the spontaneity of the process.

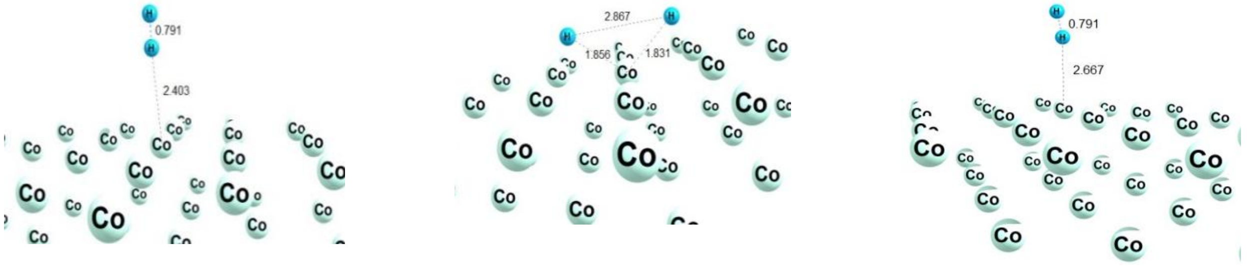
To study the activation step of the adsorption process, a Climbing Image nudge Elastic Bond (CI-NEB) method was performed to determine the transition state (TS) [6]. The total number of pixels along the reaction pathway (to be optimal until convergence) was seven. The DFT calculations and CI-NEB methods were implemented in SIESTA code [7].

RESULTS AND DISCUSSIONS

The adsorption of carbon monoxide and hydrogen on the Co(111) surface

For the adsorption of hydrogen on the Co(III) surface we considered six possible adsorption configurations (H2-1 – H2-6), which are shown in Fig. 1. In the Fig. 2 we also present the selected adsorption configurations of CO on the catalyst surface (CO-1– CO-6).

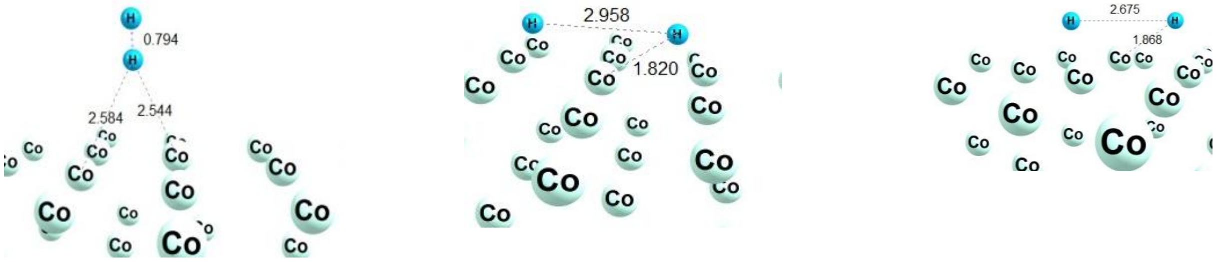
The calculated adsorption energies related to each orientation possibility of hydrogen and carbon monoxide were presented in Table 1 and Table 2, respectively.



H2-1: H_2 is oriented vertically above the Co atom

H2-2: H_2 is oriented parallel to the Co atoms

H2-3: H_2 is oriented vertically above the tetrahedral cavity

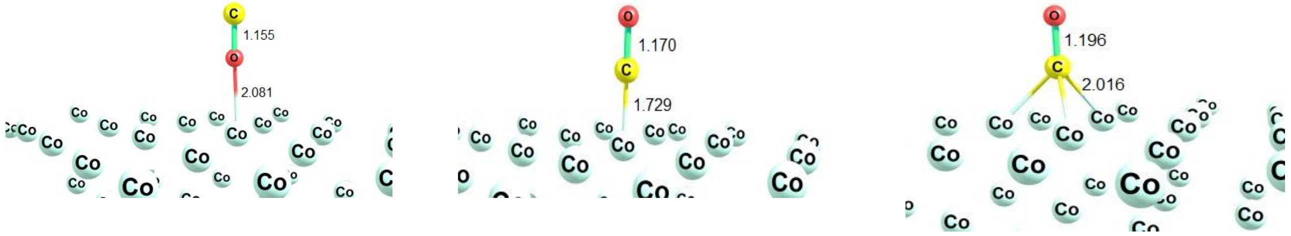


H2-4: H_2 is oriented vertically above the octahedral cavity

H2-5: H_2 is oriented horizontally above the octahedral cavity

H2-6: H_2 is oriented horizontally above the tetrahedral cavity

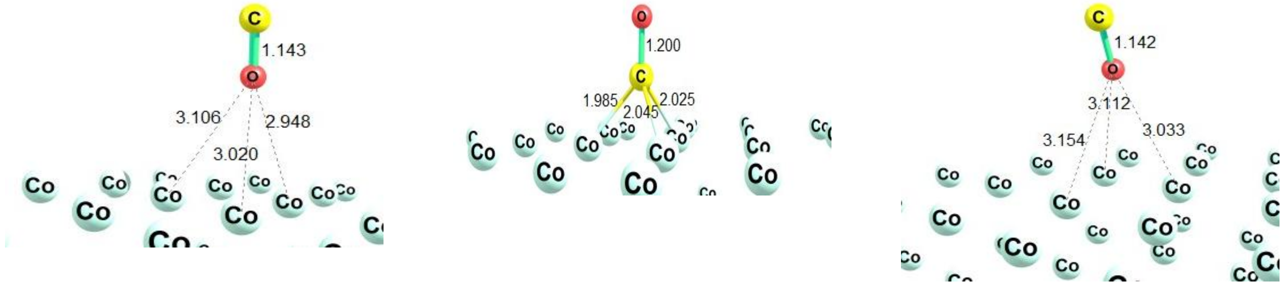
Fig. 1. The possible adsorption configurations of hydrogen on the Co(III) surface
Рис. 1. Возможные адсорбционные положения водорода на поверхности Co(III)



CO-1: CO is oriented vertically above the Co atom with the O atom down

CO-2: CO is oriented vertically above the Co atom with the C atom down

CO-3: CO is oriented vertically above the tetrahedral cavity with the C atom down



CO-4: CO is oriented vertically above the tetrahedral cavity with the O atom down

CO-5: CO is oriented vertically above the octahedral cavity with the C atom down

CO-6: CO is oriented vertically above the octahedral cavity with the O atom down

Fig. 2. The possible adsorption configurations of carbon monoxide on the Co(111) surface
Рис. 2. Возможные адсорбционные положения монооксида углерода на поверхности Co(111)

Table 1

The calculated adsorption energy of H_2 on Co (111) at DFT-GGA/PBE level

***Таблица 1.* Расчётные значения энергии адсорбции H_2 на Co (111) по DFT-GGA/PBE методу**

Configuration	E_{ads} (eV)
H2-1	-1.052
H2-2	-2.421
H2-3	-0.285
H2-4	-0.582
H2-5	-2.920
H2-6	-2.389

Table 2

The calculated adsorption energy of CO on Co (111) at DFT-GGA/PBE level

***Таблица 2.* Расчётные значения энергии адсорбции CO на Co (111) по DFT-GGA/PBE методу**

Configuration	E_{ads}(eV)
CO-1	-0.639
CO-2	-3.167
CO-3	-3.324
CO-4	-0.533
CO-5	-3.279
CO-6	-0.626

Based on the obtained data we can suggest that the H2-5 and the CO-3 are the most thermodynamically favorable adsorption configurations of H_2 and CO, respectively, due to the most negative values of E_{ads} as compared to that of the other configurations. The results also showed that the adsorptions of hydrogen and carbon monoxide are of chemical nature. Hydrogen was dissociated on the catalyst surface. The bond length between hydrogen atoms was sharply increased from 0.774 Å (for the isolated gas molecule) to 2.958 Å (for the adsorbed molecule – H2-5 configuration). Similarly for the adsorption of CO on the Co (111) structure. CO molecule was strongly bonded with the Co active site via C atom. The C-O bond length was significantly changed from 1.140 Å to 1.196 Å.

When placing CO or H_2 on Co surface from a far distance (about 5 Å), each gas molecule were still absorbed by Co. Consequently, the adsorption process of two gases does not involve the transition state. Thus, our study has shown that CO and H_2 chemically easily adsorbed on the Co (111) surface.

Conversion of carbon monoxide to methanol

According to the data presented in Tabl. 1 and 2, the adsorption energy of the most favorable adsorption configuration of Cobalt-CO (CO-3) is relatively lower as compared to that of the hydrogen. Therefore, we assume single possible pathway of methanol formation on the Co (111) as follows:

$$CO(ads) + 2H(ads) \Rightarrow COH(ads) + H(ads) \qquad (1)$$

$$COH(ads) + H(ads) \Rightarrow CH\text{-}OH(ads) \qquad (2)$$

$$CH\text{-}OH(ads) + 2H(ads) \Rightarrow CH_2\text{-}OH(ads) + H(ads) \qquad (3)$$

$$CH_2\text{-}OH(ads) + H(ads) \Rightarrow CH_3\text{-}OH(ads) \qquad (4)$$

To study the mechanism of transformation of CO to methanol on Co (111) catalyst, a climbing image nudged elastic bond (CI-NEB) method was performed to determine the transition state (TS). The initial and the final configurations as well as the transition state in each reaction step are presented in Fig. 3-6. It is assumed that the energy of the initial configurations is equal to zero. The relative energies of the seven configurations that occur in one step are also presented.

The calculated data have shown that all of steps are endothermic. The first step has the highest activation energy (E_a = 3,212 eV = 309,91 kJ/mol). This activation energy can be provided by heat. Thus, the proposed mechanism is relatively feasible.

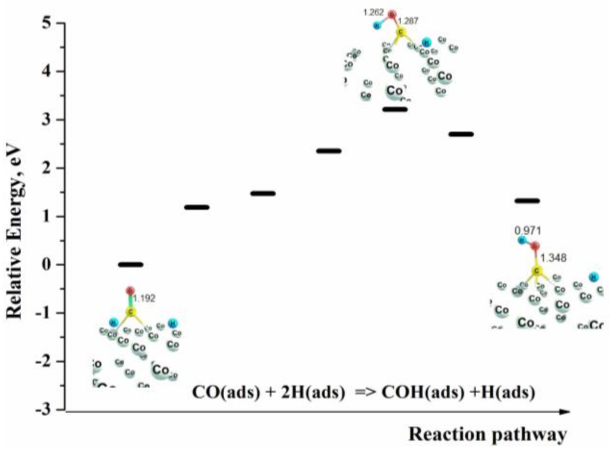


Fig. 3. Reaction pathway: CO(ads) + 2H(ads) =>
=> COH(ads) +H(ads)
Рис. 3. Ход реакции: CO(ads) + 2H(ads) => COH(ads) +H(ads)

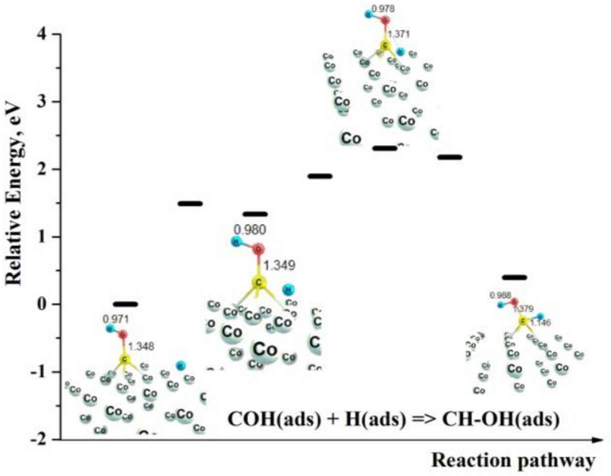


Fig. 4. Reaction pathway: COH(ads) + H(ads) => CH-OH(ads)
Рис. 4. Ход реакции: COH(ads) + H(ads) => CH-OH(ads)

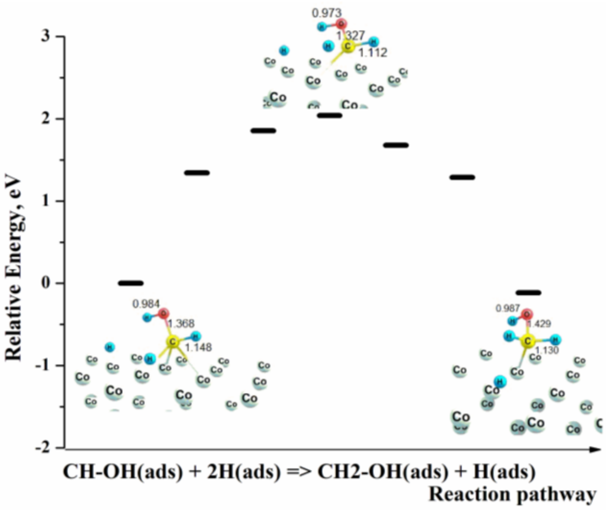


Fig. 5. Reaction pathway: CH-OH(ads) + 2H(ads) => => CH_2-OH(ads) + H(ads)

Рис. 5. Ход реакции: CH-OH(ads) + 2H(ads) => => CH_2-OH(ads) + H(ads)

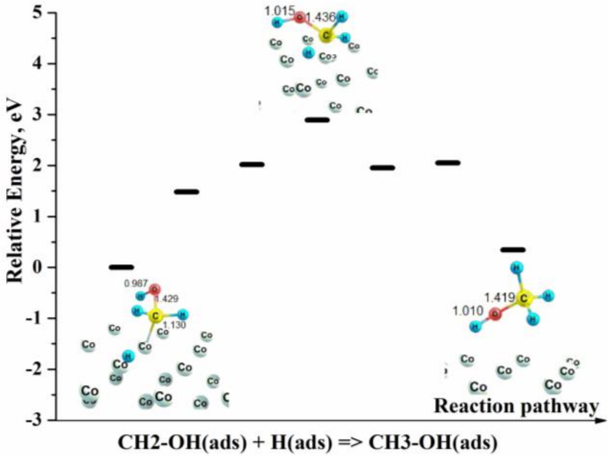


Fig. 6. Reaction pathway: CH_2-OH(ads) + H(ads) => ⇨ CH_3-OH(ads)

Рис. 6. Ход реакции: CH_2-OH(ads) + H(ads) => CH_3-OH(ads)

Table 3

The calculated activation energies (E_a) of steps 1-4 that occur during the hydrogenation of CO to methanol on the Co (111) surface

***Таблица 3.* Расчетные значения энергии активации стадии 1-4 в ходе реакции гидрогенизации CO в метанол на поверхности Co (111)**

Stage	E_a (eV)
1	3.212
2	2.310
3	2.040
4	2.447

The activation energies of each step are shown in Table 3.

CONCLUSION

In this work, we have performed a theoretical study of the hydrogenation of CO on the Co (111) surface. The theoretical methods employed for this task included density-functional theory (DFT) and a CI-NEB method. The results showed that CO and H_2 are chemically easily absorbed on the Co (111). The adsorption processes do not involve a transition state, regardless of the catalytic system considered. We also proposed a mechanism of hydrogenation of CO to methanol that was shown to be feasible due to the relative low activation energy.

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