Reaction Mechanism of CO2 Methanation

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The combustion of fossil fuels has led to a large amount of carbon dioxide emissions and increased greenhouse effect. Methanation of carbon dioxide can not only mitigate the greenhouse effect, but also utilize the hydrogen generated by renewable electricity such as wind, solar, tidal energy, and others, which could ameliorate the energy crisis to some extent. Highly efficient catalysts and processes are important to make CO2 methanation practical. Although noble metal catalysts exhibit higher catalytic activity and CH4 selectivity at low temperature, their large-scale industrial applications are limited by the high costs. Ni-based catalysts have attracted extensive attention due to their high activity, low cost, and abundance. At the same time, it is of great importance to study the mechanism of CO2 methanation on Ni-based catalysts in designing high-activity and stability catalysts.

CO2 CH4 reaction mechanism Ni-based catalysts low temperature

1. Introduction

With the continuous advancement of social economy and the unceasing enhancement of human living standards, the overuse of fossil fuels has resulted in an energy crisis while the excessive emission of CO_2 has exacerbated the greenhouse effect, which has induced global climate problems [1][2][3][4][5]. As the main component of industrial waste gas, CO_2 could also be used as an abundant and cheap chemical feedstock for renewable fuels [6]. Therefore, converting CO_2 into value-added chemicals is considered to be one of the most promising strategies to mitigate the energy crisis and reduce the greenhouse effect. Several clean and renewable energy resources such as wind, solar, and tidal energy produce discontinuous and unstable electricity, which cannot be used effectively. Hydrogen can be generated by the electrolysis of water using this kind of unstable electricity[7][8][9][10][11]. With this low cost H_2 supply, CO_2 could be hydrogenated to form methane[12][13][14][15], and methane, as the main component of natural gas, can be effectively utilized as a fuel or chemical, thus forming a new carbon cycle. In light of the importance of the CO_2 methanation reaction, it has been widely investigated. This reaction was proposed by Sabatier and Senderens in 1902, which was also called the Sabatier reaction (Equation (1))[16][17]. The reaction is exothermic, and can be carried out at low temperature to achieve high CO_2 conversion [18][19][20][21]. However, CO_2 is the upmost oxidized state of carbon and the activation of the C–O bond in CO_2 faces many challenges. The hydrogenation of CO_2 to methane is an eight-electron process with high kinetic barrier that requires a catalyst to achieve acceptable rates and selectivity[22][23][24]. The active metals usually affect the catalytic activity and selectivity of the catalysts. Many noble metals such as Rh [2][25], Ru[26][27][28], and Pd [29][30] have been widely applied in CO_2 methanation due to their excellent activity and CH_4 selectivity at low temperature. However, their large-scale industrial

applications are limited due to the high costs. In addition to noble metal catalysts, some Ni-based catalysts also exhibit high catalytic activity and CH_4 selectivity. However, the precise elucidation of the CO_2 methanation mechanism is still a challenging task. It is crucially important to understand the key intermediates and reaction mechanisms in depth when designing catalysts with excellent catalytic performance [26].

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O,\ \Delta H_{298K} = -165.4\ kJ/mol,\ \Delta G_{298K} = -130.8\ kJ/mol, \quad (1)$$

2. The Reaction Mechanism of CO_2 Methanation

Many researchers have made efforts to elucidate the possible CO_2 methanation mechanism by in situ FTIR, mass spectrometry (transient-MS) techniques, and DFT calculations. Although there are many arguments on the intermediates and different reaction pathways of CH_4 formation, two widely accepted pathways have been proposed: (1) the formate pathway where formate species are the main intermediate products formed during CO_2 methanation reaction, also called the CO_2 associative methanation: the chemisorbed $*CO_2$ species can first be converted to bidentate formates (HCOO*) and then to formic acid (HCOOH), then to CH_4, and (2) the CO pathway, also called the CO_2 dissociative methanation: the chemisorbed $*CO_2$ species can dissociate into *CO and *O. The formed *CO species can further dissociate into carbon species (*C), which can then be hydrogenated to CH_4 by dissociated H_2 still on the metal particles, desorbing from the catalyst surface, whereas the *O species can react with hydrogen to produce H_2O [10][31][32][33][34][35][36].

The possible reaction pathways are illustrated in **Figure 1**. CO_2 methanation on different catalysts occur via two different pathways, which are affected by the nature of nickel active sites and the supports [10].

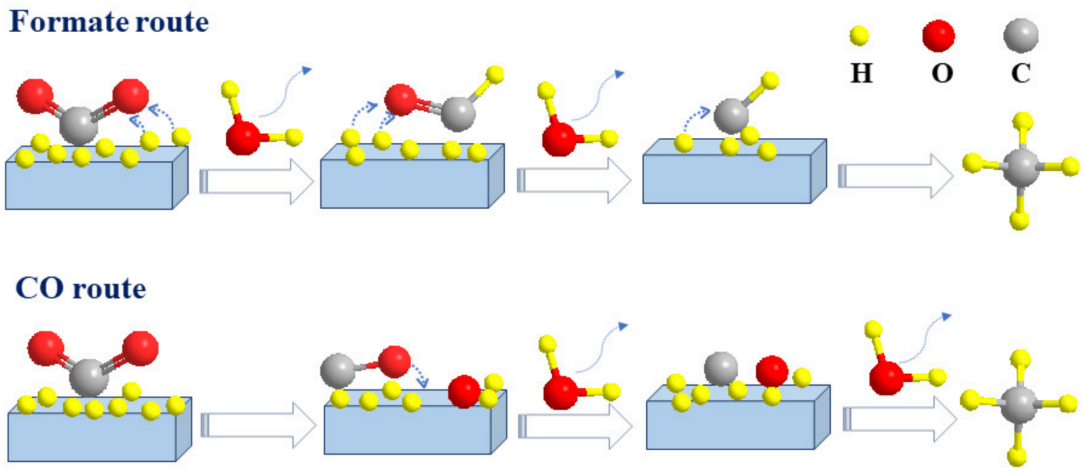

Figure 1. Two different CO_2 methanation reaction routes: formate route and CO route.

2.1. The Formate Pathway

Many studies have reported that CO_2 methanation follows the formate route on different nickel catalysts such as Ni/MgO [37], Ni-Mn/Al@Al_2O_3 [38], Ni/Y_2O_3 [39], Ni/ZrO_2 [35][40], Ni/ultra-stable Y (USY) zeolite [41], and Ni@C [42]. For

example, Xu and coworkers [35] discussed the formation and evolution of CO_2 adsorbed species on Ni/c-ZrO_2 by in situ FTIR and DFT calculations. CO_2 methanation on Ni/c-ZrO_2 was dominated by the formate pathway as follows: CO_2*→ HCOO* → H_2COO* → H_2COOH* → H_2CO* → CH_2*→ CH_4*, which is the same as that shown in **Figure 1**. CO was a by-product instead of a reaction intermediate, which could not further form CH_4, and the DFT calculations also confirmed the formate pathway, which was highly consistent with the in situ FTIR results. Solis-Garcia et al. [40] also found that CO_2 methanation follows the formate pathway over Ni/ZrO_2 and no CO species were observed during the reaction. The possible reaction pathway of the CO_2 methanation over Ni@C was also investigated by CO_2-TPD measurements and in situ FTIR characterization. All results demonstrated that CO_2 methanation over Ni@C catalyst proceeded via the formate route without involving CO as an intermediate [42]. Aldana et al. [12] also found that the main CO_2 methanation mechanism on Ni-$CZ_{sol–gel}$ was the formate pathway, which does not require CO as reaction intermediate. They also found that H_2 was dissociated on Ni^0 sites while CO_2 was activated on the ceria–zirconia support to form carbonates and then further into CH_4, suggesting that a stable metal–support interface is beneficial for the adsorption of CO_2.

In another study, Pan et al. [43] found that the reaction pathway on Ni/γ-Al_2O_3 and Ni/$Ce_{0.5}Zr_{0.5}O_2$ all followed the formate pathway, only differing in reactive basic sites. On the Ni/$Ce_{0.5}Zr_{0.5}O_2$ catalyst, CO_2 adsorption on medium basic sites formed bidentate formate, whereas CO_2 adsorption on surface oxygen resulted in the monodentate formate. Due to the faster hydrogenation of monodentate formate, it was assumed to be the main reaction route on the Ni/$Ce_{0.5}Zr_{0.5}O_2$ catalyst. For CO_2 methanation on Ni/γ-Al_2O_3, hydrogenation of bidentate formate was the main reaction route as bidentate formate was the main adsorption and intermediate species and CO_2 adsorbed on strong basic sites of Ni/γ-Al_2O_3 will not participate in the CO_2 methanation reaction. It was assumed that medium basic sites are responsible for promoting the formation of monodentate formate species, thus enhancing CO_2 methanation activity. CO_2 methanation reaction pathways on Ni/$Ce_{0.5}Zr_{0.5}O_2$ and Ni/γ-Al_2O_3 are shown in **Figure 2**.

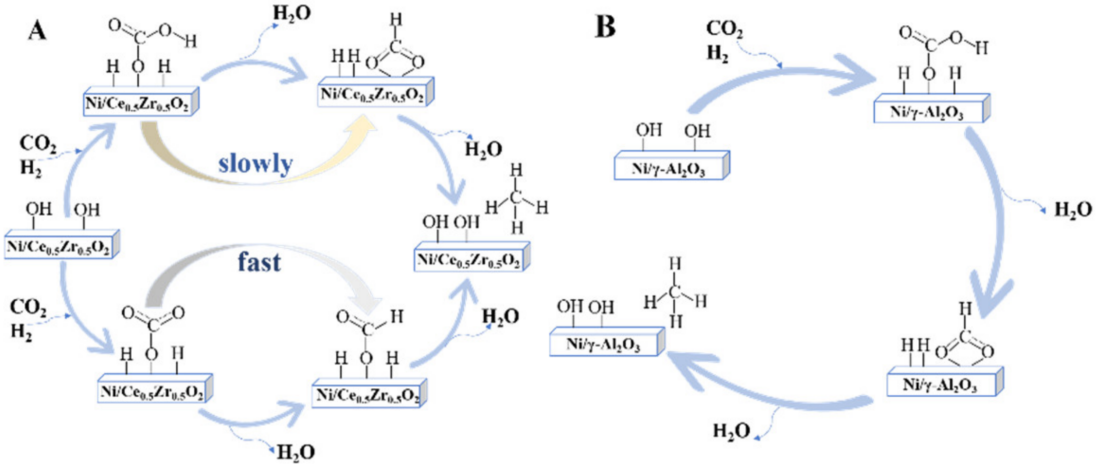

Figure 2. CO_2 methanation reaction route on (**A**) Ni/$Ce_{0.5}Zr_{0.5}O_2$ and (**B**) Ni/γ-Al_2O_3.

2.2. The CO Pathway

The CO pathway involves the dissociation of CO_2 to CO prior to methanation, and in the subsequent reaction, CO is converted to CH_4 by reacting with H_2 [44]. Karelovic et al. showed the direct dissociation of CO_2. The reactions below summarize the reduction process (Equations (3) and (4)). The excess amount of CO generated in the first reaction deposits on the catalyst, which produces coking effects. To avoid this problem, the methanation of CO must proceed much faster than the CO production, and the CO_2 methanation reaction must take place at low temperatures. Therefore, the direct dissociation of CO_2 to CO_{ads} and O_{ads} often occur over a variety of noble metal-based catalysts at low temperature [25][45][46]. In addition, the formation of nickel carbonyls $Ni(CO)_4$ would cause the deactivation of Ni-based catalysts [47].

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (2)$$

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (3)$$

Therefore, CO_2 methanation occurred via the CO pathway only over some Ni-based catalysts including Ni/CeO_2 [48], Ni/F-SBA-15 [49], and Ni-sepiolite [50]. The CO pathway over Ni/CeO_2 could be proven by in situ FTIR. The FTIR adsorption bands at 2017 cm^{-1} were assigned to the CO adsorption state, and the bands at 2120 and 2170 cm^{-1} were ascribed to gas phase CO, which indicated that CO_2 molecules can be converted to CO molecules on the surface of the Ni/CeO_2 catalyst. Characterization results indicated that CO species generated from the reduction of CO_2 molecules by nickel active sites and surface oxygen vacancies promoted CO_2 methanation [48]. Bukhari et al. found that Ni metals on Ni/F-SBA-15 (Fibrous type SBA-15) contributed to the CO_2 dissociation into CO and O species as well as the dissociation of H_2 into atomic hydrogen species. The linear carbonyl group came from the dissociation of CO_2, which was an intermediate during CO_2 methanation and could be seen at 2055 cm^{-1}. Then, the adsorbed CO species interacted with surface oxygen, producing bidentate and unidentate carbonate groups, thus CH_4 [49]. Cerdá-Moreno et al. [50] also found linearly and bridged bonded CO as intermediates during CO_2 methanation over a Ni-sepiolite catalyst.

2.3. The Key Factors of CO_2 Methanation Reaction Route

There are also many factors influencing the CO_2 methanation mechanism. The addition of promoters affects the formation of intermediates. Mg or Ca modified Ni/Al_2O_3 catalysts promote the formation of the carbonate species due to the increased basicity, while Sr or Ba modified catalysts promoted *CO and H_2CO* formation [51]. The nature of nickel active sites also influence the CO_2 methanation mechanism. Zhou et al. [52] found that CO_2 methanation took the pathway of CO over the Ni/TiO_2 catalyst with Ni (111) as the principal exposing facet, while the catalyst with multi-facets followed the formate route, with which nickel was only functional for hydrogen dissociation. The location of nickel active sites also affects the CO_2 methanation reaction pathways [33]. Controlling nickel being on either the interior or the exterior of adjacent siloxene nanosheets is achieved by employing different solvents in the preparation process, which determines the reaction intermediates and pathways for CO_2 methanation, as shown in **Figure 3**. CO_2 methanation occurred through the formate pathway over Ni@SiXNS-EtOH with nickel active sites being on the interior of adjacent siloxene nanosheets while CO_2 methanation followed the CO pathway when nickel was at the exterior of adjacent siloxene nanosheets on Ni@SiXNS-H_2O.

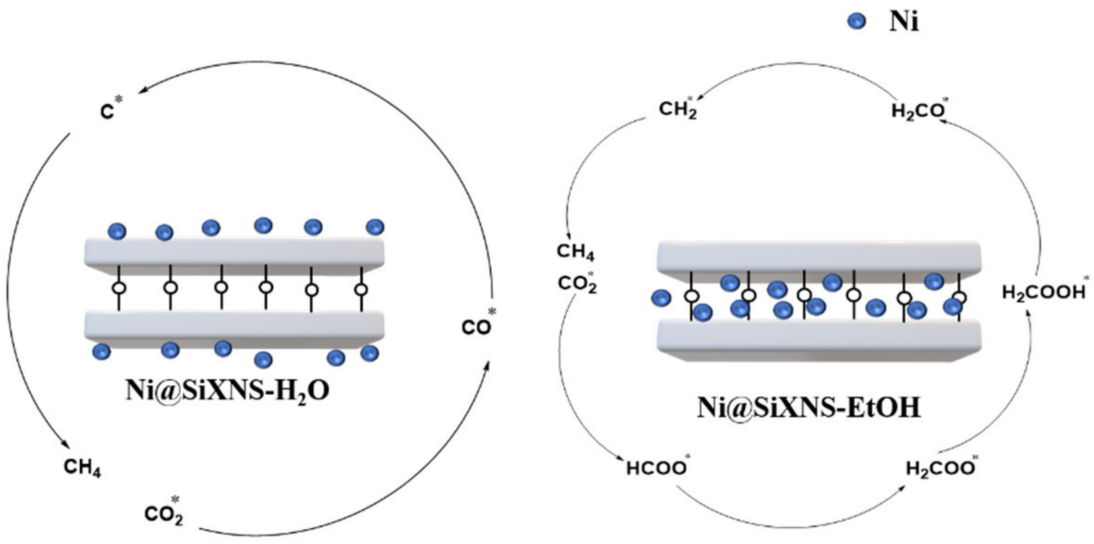

Figure 3. CO_2 methanation pathways on (**A**) Ni@SiXNS-H_2O and (**B**)Ni@SiXNS-EtOH.

The different preparation methods can also influence the reaction pathway of CO_2 methanation. Jia et al. [53] used the *operando* DRIFT analyses to demonstrate the CO_2 methanation pathway on Ni/ZrO_2 obtained via different preparation methods. CO_2 methanation over the plasma decomposed catalyst follows the Co-hydrogenation route. The exposed high-coordinate Ni (111) facets of the plasma decomposed catalyst facilitate the decomposition of CO_2 and formates into adsorbed CO. The subsequent hydrogenation of adsorbed CO leads to the production of methane. However, the thermally decomposed catalyst with a complex Ni crystal structure and more defects mainly takes the pathway of direct formate hydrogenation.

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