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Research Progress of Thermodynamic Simulation for Methane Dry Reforming

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ABSTRACT. *Methane dry reforming can produce synthesis gas suitable for Fischer-Tropsch synthesis and methanol production by utilizing natural gas or biogas rich in methane and carbon dioxide as raw material. This process is helpful for reducing production cost and energy consumption, achieving environmental protection and resource utilization. It has received more and more attention from scholars at home and abroad. Methane and carbon dioxide reforming reaction can occur spontaneously at temperatures above 640 °C. Because the reforming mechanism is not clear, there is currently no industrial production facility for carbon dioxide reforming of natural gas in China. The thermodynamic analysis can be used for investigating the reaction characteristics of methane dry reforming, and then determining the optimal reaction conditions, exploring the reaction mechanism, and guiding reactor design and industrial production. Therefore, this paper reviews the research progress of thermodynamic simulation of methane dry reforming process.*

KEYWORDS: *methane dry reforming, mechanism, thermodynamic simulation*

1. Introduction

Natural gas is one of three major fossil energy sources, and its reserves are very rich. The main component of natural gas is methane, which is used as a chemical raw material mainly in the synthetic ammonia and methanol industries, but it cannot be compared with petroleum. With the long-term exploitation of petroleum resources, their reserves are becoming increasingly scarce, and the proportion of natural gas in the world's energy structure is increasing year by year. The effective use of natural gas has attracted the attention of many researchers [1]. At the same time, greenhouse gases such as CO_2 emitted by humans into the atmosphere have increased year by year due to the direct combustion of fossil fuels since the industrial revolution, and the greenhouse effect of the atmosphere has also increased, which has caused global warming and sea level rising. Serious problems have

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greatly threatened the human living space. With the advancement of science and technology and the improvement of the awareness of human environmental protection, how to use and fix CO_2 has become a special concern of governments and researchers around the world. The carbon dioxide reforming of methane, also called methane dry reforming, can simultaneously realize the utilization of two greenhouse gases, i.e., methane and carbon dioxide. It is a synthetic gas production process with good application prospects, which turns waste into treasure, alleviates pollution and energy shortage craft.

The methane dry reforming process can produce synthesis gas with a reasonable H_2/CO ratio which can be used directly as a raw material for the synthesis of certain oxygenates. Moreover, this reforming reaction can be used as an energy storage medium and for energy transportation. This paper will discuss the mechanism of methane dry reforming and review the research progress of thermodynamic simulation of methane dry reforming.

2. Characteristics of methane dry reforming

Methane dry reforming was proposed at the 10th International Catalysis Conference. In 1928, Fiser and Tropsch first studied the dry reforming of methane [2]. In 1988, Fiser and Tropsch discovered that in the temperature range of 1033K~1273K, the catalyst utilizing Ni and Co as the active components with Al_2O_3 as an auxiliary agent has good activity for generating synthesis gas by methane dry reforming [3]. Methane dry reforming has received increasing attention due to the following advantages: (1) Methane dry reforming has a wide range of raw materials. It can simultaneously use two greenhouse gases, i.e., methane and CO_2, to produce hydrogen, alleviating the greenhouse effect caused by the two kinds of gases and reducing atmospheric pollution. (2) The H_2/CO volume ratio of the generated synthesis gas is about $\leq$1, making it particularly suitable as a raw material for oxo-synthesis and Fischer-Tropsch synthesis [4]. At the same time, it makes up for the deficiency of high hydrogen-carbon ratio ($H_2/CO \geq 3$) obtained during the conventional methane steam reforming [5]. (3) Methane dry reforming reaction has a reversible reaction with large reaction heat, so it can be used as energy storage and transmission medium. (4) Compared with traditional wet reforming and partial oxidation reforming, it can save about half of methane, with less investment, higher efficiency and lower energy consumption [6]. However, the catalyst has poor stability, and is easily deactivated due to carbon deposit during the dry reforming process of methane. The methane conversion rate is limited by the thermodynamics of the reforming reaction, and there are some problems such as high reaction temperature and high requirements on the material of the reactor. Therefore, how to improve the anti-carbon deposit ability and low-temperature activity of the catalyst is important to the industrial application of methane dry reforming. In recent years, a lot of researches around the world have been carried out on new processes, catalysts, carbon deposits and reaction mechanisms for the catalytic dry reforming of methane to produce syngas. Many meaningful results have been achieved.

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3. Mechanism of methane dry reforming

There is currently no widely recognized mechanism for methane dry reforming. The mechanism of methane dry reforming reaction is an important basis for the improvement of catalysts and the optimization of reaction process [7-10]. Many scholars at home and abroad have proposed many reaction pathways and mechanisms for the methane dry reforming [7-10]. It is generally accepted that the conversion of CH_4 is carried out by stepwise dehydrogenation decomposition at the metal center. There are two main opinions on the conversion of CO_2. On the one hand, some investigations have demonstrated that CO_2 reacts with the adsorbed hydrogen to produce water, and the water continues to react with methane by steam reforming. On the other hand, the other investigations have indicated that CO_2 is directly decomposed into CO and surface oxygen species on the metal center. The surface oxygen species then react with CH_x generated by the decomposition of CH_4 to form CO and H_2.

The first reaction mechanism was proposed in the study of steam reforming of methane on Ni foil by Bodrov and Apel Baum [11] in 1967: (where * indicates the adsorption site)

$$CH_4+*=CH_2*+H_2 \quad (1)$$

$$CO_2+*=CO+O* \quad (2)$$

$$O*+H_2=H_2O+* \quad (3)$$

$$CH_2*+H_2O=CO*+2H_2 \quad (4)$$

$$CO*=CO+* \quad (5)$$

Wei et al. [12] proposed the following reaction mechanism according to the activation process of methane and carbon dioxide:

$$CH_4=CH_{3(a)}+H_{(a)} \quad (6)$$

$$CO_2+H_{(a)}=CO+OH_{(a)} \quad (7)$$

$$CO_2=CO_{(a)}+O_{(a)} \quad (8)$$

$$CH_4+O_{(a)}=CH_{3(a)}+OH_{(a)} \quad (9)$$

$$CH_{3(a)}=CH_{2(a)}+H_{(a)} \quad (10)$$

$$CH_{2(a)}=CH_{(a)}+H_{(a)} \quad (11)$$

$$CH_{x(a)}=C+xH_{(a)} \quad (12)$$

$$CH_{x(a)}+O_{(a)}=CO+xH_{(a)} \quad (13)$$

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$$CH_{x(a)}+CO_2=2CO+xH_{(a)} \quad (14)$$

$$2H_{(a)}=H_{2(g)} \quad (15)$$

$$2OH= H_2O+O_{(a)} \quad (16)$$

Nakamura et al. [13] considered that the dissociation of CO_2 is the rate controlling step of the reaction. Kim et al. [14] found that CH4 dissociation and C-H bond cleavage are rate control steps by thermodynamic analysis, and CO_2 dissociation is preferred in comparison with the reaction of CHx species on the surface. Osaki et al. [15] considered that the reaction of $CH_{x(ads)}$ with $O_{(ads)}$ is a rate controlling step. With the deepening of research on methane dry reforming reaction and the improvement of experimental techniques and testing methods, the basic theoretical issues of the reaction, such as the active components, carriers and assistant materials of the catalyst, have become more consistent, but there is still a controversy about the deactivation of the catalyst and the reaction mechanism. But considering the complex process of methane carbon dioxide reforming, the reaction mechanism may have different modes under different catalysts and different reaction conditions.

4. Thermodynamic analysis of methane dry reforming

4.1 Methane dry reforming process

The methane dry reforming process has a very complex reaction system, and the reactions that may occur during the reaction process are shown as follows [16]:

Methane carbon dioxide reforming reaction	$CH_4+CO_2=2CO+2H_2$	$\Delta H_{298K}^0 = 247\ kJ \cdot mol^{-1}$ $\Delta G^0 = 61770 - 67.32T\ kJ \cdot mol^{-1}$	(17)
Methane steam reforming reaction	$CH_4+H_2O=CO+3H_2$	$\Delta H_{298K}^0 = 206\ kJ \cdot mol^{-1}$	(18)
Water gas shift reaction	$CO+H_2O=CO_2+H_2$	$\Delta H_{298K}^0 = -41\ kJ \cdot mol^{-1}$	(19)
Reverse water gas shift reaction	$CO_2+H_2=CO+H_2O$	$\Delta H_{298K}^0 = 41\ kJ \cdot mol^{-1}$ $\Delta G^0 = -8545 + 7.84T\ kJ \cdot mol^{-1}$	(20)

The main carbon deposition reactions in the methane dry reforming reaction system are shown as follows:

Methane cracking reaction	$CH_4=C+2H_2$	$\Delta H_{298K}^0 = 74.9\ kJ \cdot mol^{-1}$ $\Delta G^0 = 21960 - 26.45T\ kJ \cdot mol^{-1}$	(21)
Carbon monoxide disproportionation reactions	$2CO=C+CO_2$	$\Delta H_{298K}^0 = -172.4\ kJ \cdot mol^{-1}$ $\Delta G^0 = -39810 + 40.87T\ kJ \cdot mol^{-1}$	(22)
	$CO+H_2=C+H_2O$	$\Delta H_{298K}^0 = -175.3\ kJ \cdot mol^{-1}$	(23)

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According to the above reactions, when $\Delta G^0 = 0\ kJ \cdot mol^{-1}$, they will be obtained that the minimum reaction temperature of the methane carbon dioxide reforming reaction (17) and the methane cracking reaction (21), and the maximum temperatures of the reactions (20) and (22).

The following conclusions can be drawn from the above: ① When the reaction temperature is too high, methane cracking reaction may occur during the methane dry reforming process. ② When the reaction temperature is higher than 1100K, the carbon monoxide disproportionation reactions (22) and the water gas shift reaction will be inhibited. ③ Due to carbon monoxide disproportionation reactions and methane cracking reaction resulting in carbon deposits may occur at high temperatures ranging from 820K to 980K. Carbon deposit mainly is caused by the cracking reaction of methane at high temperatures. As a result, the thermodynamic equilibrium constant of the methane cracking and reverse water gas shift reaction will also increase with increasing temperature.

In addition, it can be seen from the above reactions (17) to (23) that the methane carbon dioxide reforming reaction is a strong endothermic reaction, and the reaction process is affected by various factors. The research results have shown that the reaction temperature, system pressure, feed gas space velocity and feed gas component ratio have much greater impact on the reaction process. According to the knowledge of chemical reaction, higher reaction temperature is beneficial for the methane carbon dioxide reforming reaction going in the forward direction, which promotes the conversion of methane and carbon dioxide. Thermodynamic analysis of methane carbon dioxide reforming also indicates that methane and carbon dioxide conversion rates increase with increasing reaction temperature. The space velocity of the feed gas has a great influence on the carbon dioxide reforming reaction of methane. The space velocity will directly affect the productivity of the process and the contact reaction time of the feed gas and the catalyst. The catalytic dry reforming reaction of methane is a gas-solid phase catalytic reaction. It is generally believed that gaseous methane and carbon dioxide molecules adsorb on the catalyst surface to decompose and go through reaction. The increase in space velocity may reduce the methane and carbon dioxide molecules adsorbed on the surface of the catalyst, which is not conducive to the occurrence of this reaction. Simultaneously, the study found that the volume ratio of methane to carbon dioxide in the feed gas has an effect on the reaction.

4.2 Thermodynamic analysis of methane dry reforming process

The methane dry reforming process is complicate and its reaction mechanism is uncertain, which affects the industrial production of methane dry reforming. At present, there is no industrial production equipment for methane dry reforming in China, but the simulation calculation of the reaction process can guide the production operation. There are two main methods for thermodynamic analysis of complex systems, i.e., the equilibrium constant calculation method and the Gibbs free energy minimization method. Yan et al. [17] theoretically investigated the

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effects of temperature and raw material component ratio (oxygen-carbon ratio and CO_2/CH_4 ratio) on the characteristics of methane coupling of oxygen and carbon dioxide reforming reaction based on the equilibrium constant method, and finally determined the optimal reaction temperature and raw material component ratio. The simulation results were compared with experimental results and anaerobic system. Zhang et al. [18] used lstOpt2.5 calculation software to carry out the thermodynamics analysis about methane autothermal reforming to produce synthesis gas based on equilibrium constant calculation method, and investigated the effects of temperature and raw material component ratio on the product compositions under the thermodynamics equilibrium conditions. Li et al. [19] discussed the reaction characteristics of autothermal steam and carbon dioxide reforming of methane according to the Gibbs free energy minimization method. Özkara-Aydinoglu [20] and Nikoo et al. [21] used the Gibbs free energy minimization method to calculate the methane steam reforming coupled carbon dioxide reforming. Demidov et al. [22] conducted a thermodynamic study on the methane dry reforming reaction. The Gibbs minimum free energy principle was used to determine the optimal ratio of $CH_4/CO_2/H_2O$ materials, which resulted in the lowest coke yield. Liu et al. [23] carried out calculation on the autothermal carbon dioxide reforming of methane by utilizing Gibbs free energy minimization method and computational fluid dynamics (CFD) method integrated with detailed reaction kinetics [24]. In addition, Li et al. [25] investigated the thermodynamics characteristics of methane carbon dioxide reforming by using Aspen Plus software based on the equilibrium constant method. They were explored that the effect of temperature, pressure and reaction material composition on reaction characteristics. Yang et al. [26] established a natural gas carbon dioxide reforming process model by Aspen Plus software to investigate the effects of key operating parameters such as natural gas flow rate and reaction temperature on the synthesis gas components. The optimal operating conditions were determined. Li et al. [27] also used the RGibbs Gibbs free energy reactor model in Aspen Plus to carry out methane dry reforming simulation and optimization of operating conditions. Chen et al. [28] used the equilibrium component module in HSC Chemistry software to perform thermodynamic analysis of hydrogen production from methane autothermal reforming based on the Gibbs free energy minimization method. Zong et al. [29] also used thermodynamic software HSC Chemistry software to carry out thermodynamic simulation calculation of methane carbon dioxide reforming under coke oven gas atmosphere, and studied the effect of temperature, CH_4/CO_2 ratio, pressure and carbon deposition in the process on the yield and formation law of gas products. The research results provided theoretical guidance for applying directly the syngas of the coke oven gas obtained from CO_2 reforming of methane to reduce iron ore. Yu et al. [30] also used Aspen Plus and HSC Chemistry software to perform thermodynamic simulation calculations on the partial oxidation of methane to produce syngas. They analyzed the effects of temperature, pressure and CH_4/O_2 ratio on methane conversion rate and the selection of oxygen and carbon monoxide. In addition, they also carried out thermodynamic calculations on the thermodynamic equilibrium product composition and carbon deposit reaction of partial oxidation of methane.

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5. Conclusion

As an effective way to activate methane, methane dry reforming can be used to produce alternative sources of hydrogen, which effectively alleviates greenhouse gas emissions problems, and provides renewable clean energy for humans. Methane dry reforming to produce syngas is significant in the energy and environment fields. In recent years, with the deepening of research and the improvement of experimental methods and testing techniques, there are great progresses about research on methane dry reforming to generate syngas, but there are still controversies in the reaction mechanism. Thermodynamic analysis based on equilibrium constant calculation method and Gibbs free energy minimization method is considered. The numerical calculation or thermodynamic simulation software are used to investigate the reaction characteristics of methane dry reforming, determine the optimal reaction conditions, and explore the reaction mechanism. Thermodynamic simulation analysis can guide the design of reactors and industrial production, promote the industrialization of methane dry reforming, and comprehensively improve the utilization rate of natural gas for the benefit of human.

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