



A STUDY ON THE CHARACTERISTICS OF THE REFORMING OF METHANE: A REVIEW

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ABSTRACT

Natural gas is a fossil fuel which is more suitable as raw materials for alternative energy generation. To be inserted in the global energy production as feedstock for power generation, natural gas needs to undergo a chemical technique known as reforming. The reforming of natural gas or reforming of methane, as it is also known, can be performed by different chemical techniques, each one with advantages and disadvantages with respect to cost/benefit ratio. The product of the reforming of natural gas, regardless of the process used for its realization, is a mixture of gases known as syngas. The aim of this work is to show the importance of the reforming of natural gas for alternative energy generation and analyze the differences between the methods used for the conversion of natural gas in syngas. A review of the literature on this subject is presented, including a discussion on the importance of developing the catalytic systems employed in the process of reforming of methane. Also, the challenges and future perspectives for this process have been considered.

KEYWORDS

reforming of methane; syngas; catalytic system; hydrogen; energy generation

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1. INTRODUCTION

Since the beginning of the industrial revolution in the 18th century, fossil fuels in the form of coal, oil, and natural gas have powered the technology and transportation networks that drive society. This threatens the supply of energy and causes enormous strains to the environment (Ahmed and Krumpelt, 2001).

In today's energy supply system, electricity, gasoline, diesel fuel, and natural gas serve as energy carriers. These carriers are made by the conversion of primary energy sources, such as coal, petroleum, underground methane, and nuclear energy, into an energy form that is easily transported and delivered in a usable form to industrial, commercial, residential, and transportation end-users. The sustainable energy supply system of the future features electricity and hydrogen as the dominant energy carriers. Hydrogen would be produced from a very diverse base of primary energy feedstocks using the resources and processes that are most economical or consciously preferred. Methods to produce hydrogen from natural gas are well developed and account for over 95 % of all hydrogen produced in the U.S., and 48 % globally (Hartstein, 2003; Padro and Putsche, 1999).

Natural gas is a fossil fuel, basically a mixture of light hydrocarbons, found in the basement of gas accumulations that occur in porous rocks, and may or may not be associated to oil. Natural gas is composed of saturated hydrocarbons, predominantly methane, and propane and butane in lower quantities, among other substances, like inorganic gases. In the raw state, it also has low levels of contaminants such as nitrogen, carbon dioxide, water and sulfur compounds (Thomas, 2004). Legally, by definition set out in ANP's Law No. 9.478/97, natural gas is any hydrocarbon that remains in gaseous state under normal atmospheric conditions, extracted directly from petroleum or gas reservoirs, including wet, dry, waste and rare gases (ANP, 2004). Natural gas currently is one of the best alternatives for the supply of energy and therefore urgent strategic efforts are necessary to develop alternative sources and solutions for the frequent energy shortages currently being reported (Schmal, 2005).

Today natural gas is the preferred source for production of syngas, a mixture of hydrogen and

carbon monoxide, from which purified hydrogen can be obtained. There are several different catalytic processes for producing syngas from natural gas (Armor, 2005).

In order to insert natural gas into the energy worldwide matrix as an input for power generation, this gas must be subjected to some chemical catalysts for the removal of excess carbon in its composition. Three catalytic chemical processes are used in the conversion of natural gas, composed of hydrocarbons, under a flow of high-purity gaseous hydrogen. These three catalytic chemical processes are used sequentially and are described as follows: 1. Natural gas reforming; 2. WGS process (Water Gas Shift Reaction) and 3. PROX or SELOX reaction (Preferential Reaction Oxidation of CO).

This review will discuss only the first catalytic chemical process, that is, the chemical process called natural gas reforming. This process is also known as reforming of methane and can be accomplished by means of exothermic or endothermic reactions, depending on the chemical process selected to perform the catalytic reforming of methane.

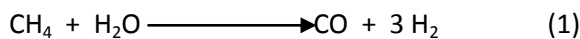
There are basically five different types of techniques that can be used to carry out the reforming of methane, namely: 1. Steam reforming; 2. Dry reforming; 3. Autothermal reforming; 4. Partial oxidation and 5. Reforming with membrane. All these types of processes have the same purpose and lead to same final product, that is, to convert natural gas, mainly composed of methane molecules, in syngas.

In order to obtain a flow of high-purity gaseous hydrogen from natural gas, it is necessary that syngas ($H_2 + CO$) be particularly obtained as a product of the reforming of natural gas when subjected to the WGS process and PROX or SELOX reactions, in this sequential order. A brief discussion on the five types of catalytic processes that can be used to carry out the reforming of methane follows.

1.1 Steam reforming

The process of steam reforming of methane produces syngas ($H_2 + CO$) with a ratio $H_2/CO = 3$. In this catalytic process, methane reacts with water steam in the presence of a catalyst. The product of

this reaction is syngas (Rostrup-Nielsen, 1984). The scheme of the reaction of steam reforming of methane is shown below.



Because the process of steam reforming of methane leads to the production of syngas with the highest H_2/CO ratio, this type of reforming process is considered ideal to obtain high-purity gaseous hydrogen.

The steam reforming of methane is an endothermic process and, therefore, requires very high temperatures, which makes his process very expensive. Therefore, research on alternative processes of methane reforming are interesting, in order to ensure economic viability according to the destination of the syngas produced. The concern with the economic viability issue led to the development of alternative processes of methane reforming, such as dry reforming, autothermal reforming and partial oxidation, which are being considered in scientific research for conversion of methane to syngas (Armor, 1999; Rostrup-Nielsen, 1984).

1.2 Dry reforming

The dry reforming of natural gas is a process whereby methane reacts with carbon dioxide in the presence of a catalyst, and syngas at a $\text{H}_2/\text{CO} = 1$ ratio is obtained (Lercher et al., 1999; Rostrup-Nielsen, 1984). The scheme of the dry reforming of methane reaction is shown below.



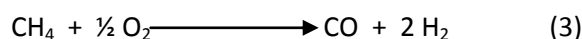
Due to the value of the H_2/CO ratio obtained in the dry reforming of methane, this process is considered the ideal type of reforming process when it comes to use the syngas produced as a raw material for the synthesis of important fuel liquids which require H_2 and CO as raw materials. On the other hand, this type of reforming process is considered very expensive because, being an endothermic process, it consumes a great amount of energy. The main disadvantage of dry reforming of methane is the significant production of by-products, typically coke, that are subsequently deposited on the surface of the catalyst, impairing its activity in the reaction. The deposition of coke on the surface of the catalyst contributes to the reduction of its useful life. The large formation of

coke occurred in this process is explained by the presence of CO_2 as a reagent. Thus, dry reforming is the unique process of methane reforming that is effected by two reagents that contain carbon (CH_4 and CO_2) (Cheng et al., 2001; Lercher et al., 1999; Rostrup-Nielsen, 1984). According to Edwards and Maitra (2000), in the reforming of methane with CO_2 there is a greater potential for carbon formation, primarily due to the lower H/C ratio of this system; on the other hand, the lower H_2/CO ratio is a preferable feedstock for the Fischer-Tropsch synthesis of long-chain hydrocarbons in some petrochemical industries.

The main challenge for the industrial application of the reforming of methane with CO_2 is related to the development of active catalytic materials, but with a very low coke formation rate, either on the catalysts or in the cold zones of the reactor. The carbon formation in this process can be controlled by using a support that favours the dissociation reaction of CO_2 into CO and O , the last species being the responsible for the cleaning of the metallic surface (Stagg et al., 1998).

1.3 Partial oxidation

The partial oxidation of methane is a catalytic process whereby methane reacts directly with oxygen in the presence of a catalyst, and the product of this reaction is syngas with a good H_2/CO ratio (Fathi et al., 2000). The scheme of the partial oxidation of methane is shown below.



The partial oxidation of methane is an exothermic process and, thus, can be considered more economic than the processes of steam reforming or dry reforming, because it requires a lower amount of thermal energy. On the other hand, partial oxidation is considered an expensive process because it requires a flow of pure oxygen. Thus, there is a warning of danger that is inherent in the process of partial oxidation of methane, since the two reagents (CH_4 and O_2) can cause an explosion if the reaction is not conducted with the necessary care (Peña et al., 1996).

1.4 Autothermal reforming

The autothermal reforming of methane is a combination of both procedures: steam reforming and partial oxidation. Thus, in the steam reforming

there is contact with a flow of gaseous oxygen, in the presence of a catalyst (**Armor, 1999**). Hence, this process of catalytic reforming of methane involves three reagents (CH_4 , H_2O and O_2).

The autothermal reforming of methane process was designed to save energy, because the thermal energy required is generated in the partial oxidation of methane. As this process consumes the thermal energy that it produces, it is called autothermal (**Ayabe et al., 2003; Wilhem et al., 2001**).

Like other reforming processes of methane, the purpose of the autothermal reforming is the production of syngas. The value of the H_2/CO ratio of the syngas obtained in the autothermal reforming is a function of the gaseous reactant fractions introduced in the process input. Typically, the value of H_2/CO ratio ranges between 1 and 2 (**Palm, 2002**).

2. COMPARISON BETWEEN THE PROCESSES OF REFORMING OF METHANE

Overall, regardless of the type of process, methane reforming is an important chemical operation in the energy worldwide matrix, because it is the first catalytic step in the conversion of natural gas, making way for subsequent chemical catalytic processes that are necessary to obtain more valuable high-purity gaseous hydrogen.

In general, the ultimate purpose of methane reforming is to obtain high-purity gaseous hydrogen; however, the type of method used in the conversion process of methane in syngas influences on H_2/CO ratio obtained. According to **Neiva (2007)**, **Armor (1999)** and **Rostrup-Nielsen (1984)**, the main type of reforming processes of methane is the process called steam reforming, because it generates syngas with the highest H_2/CO ratio. The product of the reforming process is a gas flow that is considered ideal for the development of catalytic processes to obtain high-purity gaseous hydrogen and to be used as feedstock in the petrochemical industries to produce liquid fuels and methanol. However, since the process of steam reforming is rather expensive, the other three types of catalytic chemical processes are considered as alternative processes for carrying out

the reforming of methane, and they were developed with the aim of making savings in thermal energy consumption required by these catalytic processes. Thus, the choice of the most appropriate catalytic chemical process of methane reforming must account for the economic viability of the process with regard to the destination to be given to the syngas produced. In other words, it can be said in short that the choice of the type of catalytic chemical process of reforming to be used in the conversion of methane in syngas should be made based on the final application that will be given to syngas obtained. Dry reforming, partial oxidation and autothermal reforming can also be good choices to produce syngas, if the value of H_2/CO ratio is adequate, specially when it comes to reduce the consumption of thermal energy, one of the most important factors in the implementation of an industrial project.

The cost of syngas produced by means of the steam reforming of methane process is acutely dependant on natural gas prices and is currently the least expensive among all bulk hydrogen production technologies. A well-developed natural gas infrastructure already exists in the United States, a key factor that makes syngas production from natural gas by means of steam reforming very attractive for hydrogen generation. Steam reforming of methane is widely used in industry today. Hydrogen is produced by the steam reforming of methane process in large centralized industrial plants for use in numerous applications, including chemical manufacturing and petroleum refining. Research and development programs are currently concerned with the development of small-scale technologies for steam reforming of methane to enable distribution of hydrogen and improve delivery infrastructure (**Hartstein, 2003; Padro and Putsche, 1999**).

Overall, regardless of the type of reforming process employed in syngas production, it is important to emphasize that the success of the conversion of methane is strongly dependent on the catalytic system used in the process, as well as on operational conditions such as reaction temperature. In this case one should always have in mind that the catalytic system is the material that activates the conversion reaction of methane.

3. TYPICAL CATALYTIC SYSTEMS USED IN REFORMING OF METHANE

Several types of catalysts can be used to activate the reactions of reforming of methane process. The important properties for the reforming catalyst are its activity toward reforming reaction, and its resistance toward carbon formation. The catalyst should have high thermal stability in order to maintain the reforming activity under the process conditions. In addition, the reforming catalyst should also have high resistance toward deactivation from poisoning. The major reason for the rapid decrease in the reforming activity is due to poison chemicals in the reactants or products. The poisoning of catalyst could be separated into three groups, namely the poisoning to the intrinsic activity, the poisoning to the activity of single pellets, and the poisoning to the performance of the complete reactor (Laosiripojana, 2003).

Several different transition metals can be used as catalysts in processes of reforming of methane, but nickel is the most widely used because it is the cheapest and leads to satisfactory results. Moreover, several different metal oxides can be used as catalyst supports in the processes of reforming of methane. However, the most commonly used is α - Al_2O_3 , a relatively inexpensive material with good thermal stability. In particular, thermal stability is crucial for the good performance of the catalytic system, since the process must occur at relatively high temperatures, thereby requiring that the catalytic support be refractory in order to prevent the transition metal from being founded. For the reforming of methane process, usually Ni or noble metals like Ru, Rh, Pd, Ir and Pt are used as the active metal in catalysts. Because of its low costs, Ni is the most widely used metal from this set. Common dispersions for Ni catalysts are within 2–5 % range, with metal particles of 20–50 nm. There is an optimum point beyond which an increase in Ni content does not produce any increase in activity, usually around 15–20 wt% (depending on support structure and surface). Although the nickel surface area is generally increased with higher loadings, the dispersion or utilization of nickel tends to decrease with increasing nickel content. Hence, the activity will not increase any further (Rostrup-Nielsen, 1984; Rostrup-Nielsen et al., 2002).

The influence of the catalytic support on the reforming of methane process can hardly be overrated. It not only determines the dispersion of the catalytically active metal particles or the catalyst resistance to sintering, it also affects the reactivity and coke resistance of the metal particles, and may even participate in the catalytic reaction itself. In other words, the support is a fundamental part of the catalyst and cannot be considered separately. In initial considerations, the role of the support is – literally – to provide a support for the catalytically active metal, in order to obtain a stable, large active surface area. Among the most common supports for methane reforming are α - and γ - Al_2O_3 , MgO, MgAl_2O_4 , SiO_2 , ZrO_2 and TiO_2 . These supports should have good porosity, which results in a long contact time between reactants and catalyst. Keeping a large active surface area is also important: the support can affect the migration and coalescence of metal particles, thereby causing sintering in various ways. Pore structure, morphology, and phase transitions of the support determine the final particle size of the metal. Furthermore, the electronic properties – and hence the reactivity – of the metal is affected, obviously due to the nature of the chemical bonding between the support and the metal atoms. For instance, acidity in the support is known to facilitate the decomposition of methane, but it will also promote cracking and polymerization, producing carbon. In general, a strong interaction between metal and support makes a catalyst more resistant to sintering and coking, thus resulting in a longer time of catalyst stability (Bradford and Vannice, 1996; Takatani and Chung, 1984; Wang and Lu, 1998; Zhang and Verykios, 1996). The effect of the support on the electronic properties of the catalytically active metal is also emphasized by Yokota and co-workers (2002), who reported that the support can also participate in catalytic reactions. Catalytic supports with a basic nature, such as MgO, are known to enhance the activation of steam, and allow for the dissociation of steam into OH and H species. Carbon deposits can lead to the blocking of active sites and affect the catalyst reactivity and stability. The support can also play a role in suppressing carbon deposition (Yokota et al., 2002).

Different synthesis methods can be used to develop systems for catalytic reforming of methane. According to Neiva et al. (2007; 2008), the synthesis process used strongly influences the

physical characteristics of the catalytic system finally obtained. Thus, one must choose the method of synthesis based on the best physical characteristics of the material according to the expected results.

Probably the most common technique for catalyst preparation is impregnation of a metal salt in an aqueous solution onto a support material, e.g., α -Al₂O₃. Another common method of catalyst preparation is co-precipitation. In this procedure, solutions of metal salts are added together, usually at constant pH, and precipitate into the desired product. A general treatment after the synthesis is calcination (heating the sample in air, in order to 'clean up' and 'stabilize' the catalyst) and/or reduction (heating the sample in a reducing atmosphere, usually containing hydrogen, in order to activate the catalytic metal) of the catalyst (Wang and Lu, 1998; Wang et al., 1998).

4. CHALLENGES AND FUTURE PERSPECTIVES FOR REFORMING OF METHANE

One of the major problems of the reforming of methane process is the high thermodynamic potential to coke formation (Rostrup-Nielsen et al., 2002). The catalysts based on noble metals such as Au, Pt and Ru are reported to be less sensitive to coking compared to nickel-based catalysts. However, the fact that these noble metals are expensive and of limited availability makes the development of active and stable nickel catalysts a challenge to the catalytic scientific community (Rostrup-Nielsen and Bak Hansen, 1993; Trimm, 1997).

The formation of carbon deposits is particularly undesirable in this reaction because the deposits have the form of carbon filaments, which have high mechanical strength, and the catalyst particle is destroyed when the filaments hit the pore walls. This process may result in increasing pressure drop and hot tubes. On an industrial scale, coking can be controlled by increasing steam/carbon ratios in the feed (Trimm, 1997). Several other ways of alleviating this problem have been suggested. The resistance of nickel catalysts to coking can be increased by modifying the type of the support (Bradford and Vannice, 1996; Gadalla and Bower,

1988) or introducing promoters and additives (Rostrup-Nielsen, 1984). The addition of small amounts of sulfur (Choudhary et al., 1998), alkali and rare earth oxides (Horiuchi et al., 1996; Zhuang et al., 1991) or MoO₃ seems to be effective in preventing coke formation. However, the application of these promoters causes, in most cases, a considerable decrease in the specific activity of nickel (Borowiecki et al., 1997).

According to Padro and Putsche (1999) and Hartstein (2003), the reforming of methane is a mature technology, which makes it especially important to start the transition to a hydrogen energy economy. However, the problem with the steam reforming of methane is that it operates at or near its theoretical limits. The syngas produced for hydrogen generation is still expensive compared to cost targets in the production of hydrogen for petrochemical industries. Additional research and development is needed to identify more durable reforming catalysts; improve reforming efficiencies; develop advanced shift, separation, and purification technologies; and reduce the cost of carbon capture and sequestration. Finally, natural gas is used in many other sectors of the U.S. economy, including the commercial, residential, and electric generation sectors. If natural gas is used for hydrogen production, and the demand of natural gas in other market sectors continues to grow, the natural gas reserves would decrease and the supply would be put under greater pressure. This could result in increased natural gas prices. Strong efficiency improvements in existing natural gas markets are therefore critical to keeping methane gas affordable for syngas production destined to the production of high-purity hydrogen.

Haryanto et al. (2005) affirm that hydrogen is considered to be the most viable energy carrier for the future. Producing hydrogen from steam reforming of methane would not only be environmentally friendly, but would also open new opportunities for utilization of nature resources, which are globally available.

Alternative energy generation is paramount to the socioeconomic development of a country or region. Somehow, it is present in the entire chain of production, distribution and consumption of goods and services. Equally important is the role of technology in the balanced and sustainable

development of various economic sectors, especially energy generation. The more it brings new knowledge and technology to a product or service, the higher its market value and its benefits to society, such as generating skilled jobs, improving the distribution of income and quality of life, impelling the economy and increasing the country's sovereignty (Pompermayer, 2009).

5. CONCLUSIONS

With the growing concern of environmental preservation in the present days, the future prospects for the use of natural gas show a large increase in the recovery of fuel and raw materials for alternative energy generation. According to the literature review presented in this work, we conclude that each chemical process of reforming of methane presents its particularities and the choice of the type of method to be used in the conversion of the methane into syngas should be made based on the final application that will be given to the syngas obtained. It can be concluded that the process of steam reforming leads to the production of syngas with the highest H₂/CO ratio; however, this method presents high costs because it involves a highly endothermic process. In general, one can say that choosing the best method for reforming of methane should consider the cost/benefit ratio. Furthermore, the chemical and physical characteristics of the catalytic system have fundamental importance for the success of methane conversion. However, nickel catalysts are the most used materials in the process of reforming of methane because of their low cost compared to noble metals, which could also be used in such catalytic application. It can also be asserted that the final structural characteristics of the catalytic system depend strongly on the methodology employed in the preparation of the catalyst. Such characteristics affect the performance of the catalytic system. Furthermore, it can be concluded that the catalytic support contributes to the conversion reaction of methane by means of chemical interactions with the active catalytic metal deposited on the support. The challenges of the reforming of methane process involve the development of novel research aiming to optimize this catalytic process, such as the development of new catalytic materials that are more resistant to deactivation, and the

development of better operating conditions aiming to reduce the cost of that process, bearing in mind that the process of reforming of methane has its guaranteed place in future technological developments related to the use of natural gas for energy generation.

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