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## The importance of natural gas reforming

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### 1. Introduction

Natural gas is a fossil fuel found in nature reserves, associated or not with petroleum. Its composition is a mixture of light hydrocarbons, generally alkanes, which are normally gaseous at room temperature. Methane is the most abundant gas, accounting for more than 85% of the natural gas, and the other constituents are light alkanes such as ethane, propane, butane, among others. The percentages of each constituent of natural gas vary depending on factors such as geological formation of the reservoir rock, as well as the type of organic matter that gave rise to the natural gas found. Recently, natural gas has attracted the interest of many researchers and the large amount of methane contained in natural gas has been considered an input in the production of other high-value products such as syngas and high purity hydrogen. Considering the global trend toward environmental preservation, which emphasizes clean and sustainable energy generation, it can be said that the interest of researchers for natural gas will increase significantly from now on (Odell & Rosing, 1983).

The interest in natural gas is directly related to the search for alternatives to replace petroleum-based fuels and for generating energy from sources less aggressive to the environment. This behavior resulted in the intensification of research and exploration, particularly among developing countries. The result was not only the increase in proven oil reserves but also in its geographic expansion (the existence of reserves and the possibility of their exploitation must be proven by tests). Until 1970, these reserves were concentrated in a few regions of the world, like North America and the former Soviet Union (ANEEL, 2008).

Awareness of the imminent scarcity of oil in the next decades is stimulating the search for a fuel that can partially replace petroleum-based fuels. Worldwide reserves of natural gas are under-exploited because they are not as valuable as the petroleum reserves. In some cases, when natural gas is associated with oil reserves, while the valuable petroleum is fully exploited, the associated gas of the same reserves is considered undesirable, volatilized into the atmosphere or burnt in the platform's flare. Fortunately, though, this situation is gradually changing, and natural gas is getting more attention, due to the growing need to produce hydrogen from hydrocarbons. Among the fossil fuels, natural gas is the most suitable for this application (Fishtik et al., 2000).

Energy generation is fundamental 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 power 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).

Meeting the energy demands has been a constant challenge for many countries, especially the least developed. Aware of this, Brazil has invested considerable resources in infrastructure and power supply, and has developed important technologies in specific segments such as hydroelectric power generation, transmission over long distances and integration of new electrical systems. This leadership has proved to be essential and will remain important to Brazil, but we must go further. In this new business context, we must be able to provide quality, safe, environmentally sustainable and low-cost energy services that require more leadership in specific segments. We need a broad technology-based supply chain of the energy sector, which includes electronics and nanostructured materials, among other items that involve technologies which are a privilege that few countries have afforded (Pompermayer, 2009).

In order to use natural gas to produce a clean fuel like high purity hydrogen to fuel cells for electric energy generation it is first necessary to bring natural gas to a catalytic process called natural gas reforming. This catalytic process is also known as reforming of methane. Natural gas reforming is based on a catalytic chemical reaction that aims to convert methane, the main constituent of natural gas, in a mixture of hydrogen and carbon monoxide. This mixture of gases ( $H_2 + CO$ ), the product of natural gas reforming, is called syngas. Syngas is commonly used in the synthesis of important products of the petrochemical industry such as methanol and ammonia (Rostrup-Nielsen, 1984; Armor, 1999).

In this chapter, we set out the general approach we adopted concerning the importance of natural gas in the worldwide energy matrix, and also on the basic principles that guide the reforming of natural gas catalytic processes.

## 2. History of the Use of Natural Gas as Fuel

The use of natural gas by ancient civilizations (1000 BC) to make fire to light candles in religious temples or to fire kilns to bake ceramics is widely reported in the literature.

At the end of the XIX century, natural gas was already used in North America as a fuel to generate thermal energy for heating homes and other applications such as cooking. Since then, the use of natural gas has increased and was present in several areas, such as welding processes and other processes in the metallurgical industry, water heaters, illuminator place, clothes dryers, in addition to the applications already mentioned. Thus, natural gas has spent decades, throughout of the XIX and XX centuries, being used as fuel for generating thermal energy of various forms (Olah et al., 2006).

The use of natural gas as fuel has become even more widespread when its transport and storage processes were mastered and became more reliable. Large quantities of natural gas have already been lost during the processes of petroleum and gas extraction, and this is still happening today. In many cases, when the unique purpose of a platform is to extract petroleum from a reserve, the associated gas found in the same reserve is considered as a byproduct of the petroleum extraction process. This natural gas considered an undesirable byproduct is often released into the atmosphere or burnt in the platform of extraction.

Natural gas has been growing on the worldwide scenery after the discovery of its great potential for generating electricity. Thereafter, this fuel began to attract the attention of researchers, industry and environmentalists (Hoffmann, 2002). As a consequence, some developed countries began to recognize natural gas as a highly valuable raw material to be used in energy generation.

Since environmental preservation has become a major global concern, alternative sources of energy generation must be sought, so that the growing worldwide energy demand is met without damage to the environment, particularly with respect to the minimization of the major factors of global warming.

Currently, water and petroleum are considered the main fuels for power generation worldwide. However, these fuels are natural resources that are getting scarce and because they are so valuable and non-renewables it is of is vital and urgent studies related to the development of alternative forms of energy generation.

Within this context, natural gas is believed to be the most appropriate fossil fuel to generate electricity in an alternative and sustainable form, that may help preserve the natural reserves of water for more noble and humanitarian applications.

### 3. The growing need for extraction of hydrogen from hydrocarbons

Hydrocarbons are formed by molecules made up of carbon and hydrogen atoms. Methane, the simplest hydrocarbon molecule ( $\text{CH}_4$ ) is the main constituent in natural gas. In the methane molecule, a single carbon atom is surrounded by four hydrogen atoms. Besides methane, the gas composition contains other light hydrocarbons such as ethane, propane, butane, and so on. Figure 1 shows two examples of constituent molecules of the hydrocarbons in natural gas. Hydrocarbons may have direct or branched-chain molecules. Carbon can also form multiple bonds with other carbon atoms, resulting in unsaturated hydrocarbons with double or triple bonds between carbon atoms (Olah et al., 2006).

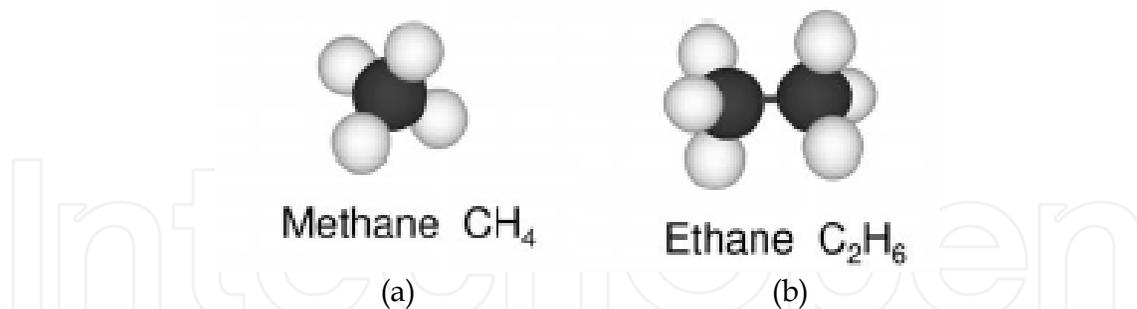


Fig. 1. Examples of main components of natural gas. (a) Methane; (b) Ethane (Olah et al., 2006).

All fossil fuels, natural gas, oil and coal, are basically composed of hydrocarbons, but they differ significantly regarding the number of hydrogen atoms and carbon atoms in their molecules. The main constituent of natural gas is methane (typically at concentrations above 80-90%) but are also found in varying proportions ethane, propane, butane, carbon dioxide, nitrogen, water, hydrochloric acid, methanol, and others. The proportion of each constituent in the final composition depends on a number of natural variables such as the formation and accumulation conditions in the reservoir (Odell & Rosing, 1983; ANEEL, 2008).

Hydrogen can be produced from hydrocarbons by their reforming or partial oxidation. Compared to other fossil fuels, natural gas is the most appropriate input for hydrogen production because of its availability for this purpose compared to oil, and also because it has the highest ratio hydrogen to carbon ratio, which minimizes the amount of CO<sub>2</sub> produced as a byproduct. Methane can be converted into hydrogen by steam reforming or dry, or by means of partial oxidation, or by both processes performed in sequence (Autothermal reforming). Steam reforming is the preferred method, which represents 50% of the global processes of conversion of natural gas for hydrogen production. This percentage reaches 90% in the U.S. In this process, natural gas (methane) reacts with water in vapor form in the presence of a metal catalyst in a reactor under high temperature and pressure conditions to form a mixture of carbon monoxide (CO) and hydrogen as reaction product, this product mixture being called synthesis gas. In a subsequent catalytic process for the reform process, the flow of hydrogen contaminated with CO will be oxidized to produce CO<sub>2</sub> and hydrogen as products. In this purification process, the hydrogen is recovered, while the byproduct CO<sub>2</sub> is generally volatilized to the atmosphere. In the future, however, the CO<sub>2</sub> shall be captured and isolated, Obec the environmental protection measures that support the control or combat global warming. The concept of producing hydrogen from oil, although established, is not attractive, since it is not expected to meet the global demand for energy in the long run, due to the scarcity of oil reserves. Coal, with the largest reserves among all other fossil fuels, may provide significant amounts of hydrogen, and the current technology to achieve this goal is called integrated gasification combined cycle (IGCC). As it occurs in the reforming of methane, coal is gasified by partial oxidation at high temperature and pressure. The synthesis gas generated in a mixture containing mainly CO and H<sub>2</sub> (also CO<sub>2</sub>) must be subsequently subjected to catalytic processes to treat CO and, thus, purify the hydrogen stream. However, as coal has a low ratio of hydrogen / carbon, the process of obtaining hydrogen from coal would lead to a greater production of CO<sub>2</sub> by methane or even oil. A great amount of energy is required for the processes of capture and sequestration of CO<sub>2</sub>, which makes it very expensive, and consequently, avoided by the industries of this area (Romm, 2004).

#### 4. The Reforming of the Natural Gas

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. Thus, three catalytic chemical processes are used in the conversion of natural gas, composed of hydrocarbons, in a gas hydrogen flow of high purity. These three catalytic chemical processes are used sequentially and are as follows, respectively: 1. Natural gas reforming; 2. WGSR process (Water Gas Shift Reaction) and 3. PROX or SELOX reaction (Preferential Reaction Oxidation of the CO).

This chapter will discuss only the first catalytic chemical process, that is, the chemical process called natural gas reforming.

Natural gas reforming also known as reforming of methane can be accomplished by means of an exothermic or endothermic reaction depending on the chemical process selected to perform catalytic reforming of methane.

There are basically four different types of processes that can be used to carry out the reforming of methane. They are: 1. Steam reforming; 2. Dry reforming; 3. Autothermal

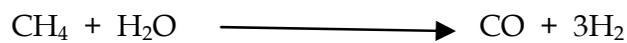
reforming and 4. Partial oxidation. All these four types of reforming of methane processes have the same purpose and lead to same final product. The purpose of the reforming of methane process, whatever it is, is to convert natural gas, mainly composed of methane molecules, in syngas. The product of the reforming of methane, the syngas, is a mixture of hydrogen and carbon monoxide.

In order to obtain a gas hydrogen flow of high purity from natural gas it is necessary that the syngas ( $H_2 + CO$ ) obtained as a product of the reforming of the natural gas process be subjected to the two previously mentioned catalytic chemical processes: WGSR process and PROX or SELOX reaction, in this sequential order.

A brief approach on the four types of catalytic chemical processes that can be used to carry out the reforming of methane follows.

#### 4.1. 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 the 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 is the reforming process that leads to the obtaining of syngas with the major  $H_2/CO$  ratio, this type of reforming process is considered ideal to obtain a gas hydrogen flow of high purity from syngas.

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 to reforming of methane to ensure the economic viability according to the destination of the syngas obtained would be interesting. The concern with the economic viability issue led to the development of alternative processes to reforming of methane, such as dry reforming, autothermal reforming and partial oxidation, which are being considered in scientific research for conversin of methane to syngas (Rostrup-Nielsen, 1984; Armor, 1999).

#### 4.2. Dry Reforming

The dry reforming of natural gas is a process where methane reacts with carbon dioxide in the presence of a catalyst, and syngas at a  $H_2/CO = 1$  ratio (Rostrup-Nielsen, 1984; Lercher et al., 1999) is obtained as a product of this reaction. The scheme of the dry reforming of methane reaction is shown below.



Due to the value of the  $H_2/CO$  ratio shown by the syngas 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 formation of structures (coke) that are subsequently deposited on the surface of the catalyst that is active 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 the CO<sub>2</sub> reagent introduced in the catalytic process input, the share of CO<sub>2</sub> reagent increasing the production of coke. Thus, dry reforming is the unique process for reforming of methane powered by two reagents that contain carbon (CH<sub>4</sub> and CO<sub>2</sub>) (Rostrup-Nielsen, 1984; Cheng et al., 2008; Lercher et al., 1999).

#### 4.3. Partial Oxidation

The partial oxidation of methane is a catalytic process in which methane reacts directly with oxygen in the presence of a catalyst, and the product of this reaction is the syngas which is shown with a H<sub>2</sub>/CO good 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, considered more economic than the processes of steam reforming or dry reforming, because it requires a smaller amount of thermal energy. On the other hand, the partial oxidation is considered an expensive process because it requires a flow of pure oxygen. Thus, there is a warning of danger inherent in the process of partial oxidation of methane, since the two reagents (CH<sub>4</sub> and O<sub>2</sub>) can cause an explosion if the reaction is not conducted with the necessary care (Peña et al., 1996).

#### 4.4. 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 gas oxygen flow, in the presence of a catalyst (Armor, 1999). Hence, this process of catalytic reforming of methane involves three reagents (CH<sub>4</sub>, H<sub>2</sub>O and O<sub>2</sub>).

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<sub>2</sub>/CO ratio of the syngas obtained in the autothermal reforming is a function of the gaseous reactant fractions introduced in the process input. Thus, the value of H<sub>2</sub>/CO ratio can be 1 or 2 (Palm, 2002).

#### 4.5. Comparison between the types of reforming of methane

Overall, regardless the type of process, the reforming of methane is an important chemical operation in the energy worldwide matrix, because this chemical process is the first catalytic step of the natural gas conversion to make way for the subsequent chemical catalytic processes necessary to obtain the valuable gas hydrogen flow of high purity.

According to the definitions presented in this chapter for the four types of reforming processes of methane, it was found that the main type of reforming is the process called steam reforming, because it has the greatest value for  $H_2/CO$  ratio, ie, the product of the reforming process is a gas flow considered ideal for the development of the catalytic process of obtaining a gas hydrogen flow of high purity. However, as the process of steam reforming is considered too 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 for catalytic process to occur. The choice of the catalytic chemical process type to reforming of methane must take into consideration the economic viability of the process related to the destination to be given to the syngas produced as a product, ie, in general the ultimate purpose is to obtain a gas hydrogen flow of high purity. The types of catalytic processes of reforming of methane called partial oxidation and autothermal reforming are good choices to produce syngas when the value of  $H_2/CO$  ratio is adequate and specially when it comes to reduce the consumption of thermal energy, a most important factor. In short, it can be said that the selection of the type of catalytic chemical process of reforming of methane depends on the type of application of the syngas produced.

## 5. Catalysts commonly used in the reforming of methane

Reports on the development of scientific research involving the use of catalysts on noble metal supported in metal oxides to carry out reforming of the methane are widely reported in the literature.

The main noble metals used in catalytic processes of reforming of methane are Pt, Rh, Pd and Ru, according to scientific publications. Each noble metal considered individually has characteristics and peculiarities when submitted to the reaction conditions of the reforming of methane processes (Seo et al., 2002; Wang et al., 2005; Bulushev & Froment., 1999). Therefore, scientific research is essential to define the catalytic action of each active species individually analyzed, showing the strength points in their catalytic performance as well as stressing their limitations, such as restrictions on activity, selectivity limits, low thermal stability, among others. Thus, in general, the published scientific studies are unanimous in stating that the noble metals, particularly Pt and Rh metals, are excellent for use as active species in catalytic reforming processes of the methane. These are ideal for this application because they have the exact catalytic characteristics that are necessary to reaction conditions of the reforming of the methane process. The characteristics of the catalytic performances of noble metals that make them so valued for this application are: high activity, ie, the great high capacity of methane to convert in syngas, good thermal stability, good selectivity and high resistance to deposition of coke on its surface, this latter characteristic helps increase the lifetime of the catalyst. The use of noble metals, particularly Pt and Rh as active species for catalytic reforming of the methane processes attract much interest because they lead to excellent results. However, they are very expensive (Hickman & Shimidt, 1992; Monnet et al., 2000; Fathi et al., 2000).

Through scientific research was discovered that Ni when tested under reaction conditions of reforming of methane process, the catalytic performance and the quality of the product output are equivalent to the final results obtained by noble metals such as Pt and Rh. Thus, the Ni has attracted much interest from researchers, because this metal exhibits the catalytic

performance of a noble metal combined with the advantage of low cost. Thus, regardless of the type of reforming of the methane process, Ni is considered the main active catalytic species to convert methane in syngas. The Ni can be considered a classic catalyst for the reforming of methane processes (Seo et al., 2002; Tornaiainen et al., 1994; Eriksson et al., 2005).

However, the catalytic system that operates in the reaction is not solely formed by the active catalytic species. In order to incorporate the active catalytic species, the catalyst system needs a catalytic support for the active species. Thus, the catalytic system consists of two components of equal importance: the active catalytic species also known as active catalytic phase and catalytic support.

The active catalytic species consists of a noble or non-noble metal in the reforming of the methane process, usually Ni, and the catalytic support consists of a metal oxide. The function of the catalytic support is to assist the active species so that their catalytic action is undertaken, ie, the active species can not perform its catalytic action alone. The catalytic support acts as a material substrate where the catalytically active species must be physically supported to act.

The catalytic systems are generally composed of active catalytic species + catalytic support. They are usually represented as follows: metal/metal oxide. Example: Ni/Al<sub>2</sub>O<sub>3</sub>.

### 5.1. Importance of the structural characteristics of the catalytic system

The process of steam reforming, the main type of catalytic process of reforming of methane involves a highly endothermic reaction that reaches very high temperatures, in most cases varying between 700 and 1000°C (Rostrup-Nielsen, 1984). Thus, the catalytic system (active species + catalytic support) of this process must be refractory to ensure the thermal stability of the catalytic system. In this case, the aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) is a good option to be used as catalytic support, because this oxide is highly refractory, supports inert form values of temperatures above 1000°C. Therefore, there are many scientific publications on its use as catalytic support for reforming of methane processes. However, other oxides can also be used as supports for catalysts for reforming of methane. The scientific publications on the issue generally report the use of different oxides such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZnO and others as catalyst supports, though the use of Al<sub>2</sub>O<sub>3</sub> is the most common, certainly due to its ability to promote the thermal stability of catalytic chemical processes.

Since the catalytic chemical process of reforming of methane involves tough operating conditions, special attention must be paid to the characteristics of the catalytic refractory support to avoid or minimize the sintering of active species. The sintering of active species is one of the factors that lead to the deactivation of the catalyst, so it must be fought with the use of catalyst refractory supports. Nevertheless, the selection of the type of catalytic support material must be made according to the catalytic process in which this support will act. For example, if the catalytic process requires a large amount of oxygen to occur, it is preferable to use a metal oxide capable of storing oxygen in its atomic structure, e.g. CeO<sub>2</sub>, as catalytic support.

Most times, the catalytic support may consist of a mixture of metal oxides. In general, two oxides are mixed in a doping process, where an oxide is used as host matrix for the incorporation of the second oxide that will be used as the dopant substance of the support. In these cases, the selection of the metal oxides to form the mixture is based on their individual characteristics. The purpose of mixing a metal oxide with another one to

compose a catalytic support is to optimize the performance of the catalytic system as a whole. It has been exhaustively proven in scientific publications that certain compounds or substances (metal oxides) incorporated with other types of oxides, have a positive influence on the outcome of the catalytic process. Thus, optimizations such as increases in activity, selectivity and resistance to coke deposit are observed (Carreño et al, 2002; Neiva, 2007; Neiva et al., 2009).

Some metal oxides are more suitable to the optimization of the catalytic system. As demonstrated by Neiva (2007) in a study involving the addition of  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CeO}_2$ , as doping substances in the catalytic system  $\text{Ni}/\text{Al}_2\text{O}_3$ , the oxide that most favored the optimization of the catalytic activity was  $\text{ZnO}$  added in a concentration of 0.01 mol in the structure of the catalytic system  $\text{Ni}/\text{Al}_2\text{O}_3$ . The present study stresses the importance of the concentration value of the doping substance added to a catalytic system, which must be within a given range of values. If the concentration of the doping substance exceeds this limit the catalytic activity of the system may be harmed. Also, according to the research carried out by Neiva (2007), a comparison of the catalytic activity of the system (1.5%)  $\text{Ni}/\text{Al}_2\text{O}_3$  doped with the following oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CeO}_2$  is shown in figure 2. According to the graphs of Figure 2, the catalytic system (1.5%)  $\text{Ni}/\text{Al}_2\text{O}_3$  doped  $\text{ZnO}$  showed higher catalytic activity, ie, higher peaks of methane conversion. These catalytic systems with the performances shown in Figure 2 were synthesized by the combustion method.

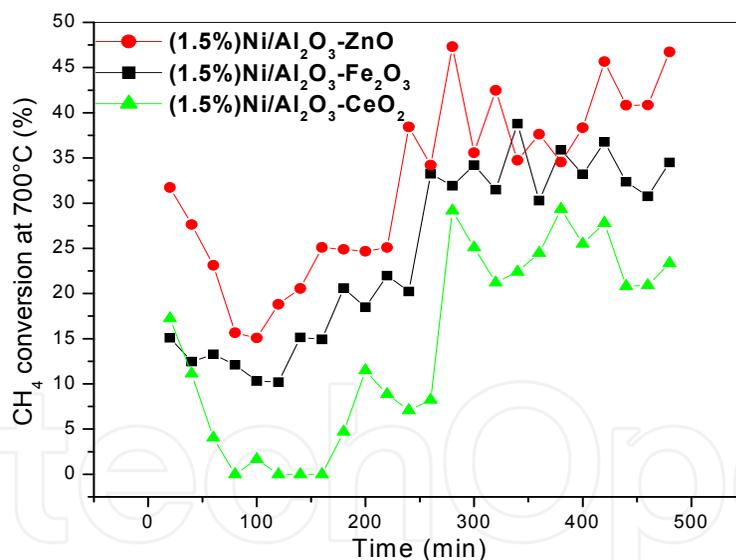


Fig. 2. Comparison between the performances of the catalytic system  $\text{Ni}/\text{Al}_2\text{O}_3$  doped with the oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{CeO}_2$  in the reforming of the methane reaction held at  $700^\circ\text{C}$  (Neiva, 2007).

In general, these catalytic supports consisting of more than one oxide are called doped or modified catalytic supports. Is called of dopant substance or dopant element of the catalytic system the metal oxide added in small quantities in the atomic structure of metal oxide which is most of the support structure, ie, inside of the hospitable matrix structure. The

functions of the two metal oxides, dopant substance and host matrix are defined in the reforming of the methane catalytic process.

The stages formed by the dopant substance are active phases that optimize the catalytic activity of the system as a whole, by helping the catalytic action of the main phase that was deposited on the support doped or modified (Neiva et al., 2008).

The atomic structure of the doped or non-doped catalytic support must have a porosity suitable to the deposition of the active catalytic species on the support and also should allow that active species have a satisfactory performance in the catalytic process. The active species should be deposited on the porous structure of the catalytic structure as smoothly as possible, so that the catalytic activity is carried out all along the catalytic system and not merely in isolated points. Catalyst supports that have highly crystalline atomic structures favor the occurrence of deposition with very homogeneous dispersion of the active catalytic species (Figueiredo & Ribeiro, 1987; Neiva, 2007).

## 5.2. Synthesis of catalytic systems for reforming of the methane

Currently, it is possible to develop catalytic supports with controllable physical and structural characteristics. Thus, we can affirm that physical characteristics such as type of porosity, degree of crystallinity and particle size are a function of the type of synthesis method employed in the process of obtaining the metal oxide. Also, these structural characteristics are strongly dependent on the preparation conditions used in the synthesis process, such as the type of precursor chemical used and the possible heat treatments (Neiva, 2007).

The catalytic supports formed by a unique metal oxide or a mixture of oxides usually occur in the form of a ceramic powder made by smaller particles. In some cases, the referred powders are composed of nano size particles. Thus, in general, the synthesis methods used to prepare the catalytic supports are the same methods used in the synthesis of ceramic powders. The synthesis methods commonly used for the development of catalytic supports are called combustion reaction, Pechini method and co-precipitation method. Of these, the most versatile is the method of combustion reaction, because it is faster, more efficient and can be performed from any heat source, such as a hot plate, conventional oven, microwave oven, among others. The great advantage of this synthesis method is its fastness, because the synthesis of a ceramic powder sample obtained by using the combustion reaction method lasts in average 5 minutes. Consequently, the ceramic powder final product has small-sized particles that can reach the nano scale, which represents an advantage in catalysis. Since the catalytic chemical processes involve adsorption of gases, the use of small particles such as nano is recommended, because small-sized particles have a greater contact area between the adsorbent (particle) and adsorbate (gaseous reactants of the catalytic reaction). On the other hand, the combustion reaction synthesis method is not the method of synthesis of ceramic powder most suitable for the development of catalysts for the reforming of the methane process, because since it does not include a thermal treatment such as calcination to remove undesirable elements aggregates, the ceramic powder obtained as final product of this synthesis method contains highly contaminated waste arising from the carbon precursor used as fuel in the combustion reaction. Such waste carbon will interact with the reagents of reforming of the methane process and, as a consequence, will significantly increase the formation of coke, strongly contributing to the deactivation of the catalyst. The utilization of chemical methods for nanosize particles preparation, with physical chemical

properties and wished structural has been being the main focus of several researchers in different areas of the science and technology, due to the molecular stability and good chemical homogeneity that can be reached. These methods, also enable a good control in the particle size form and distribution and/or agglomerates. Among lots of existing chemical methods, the synthesis for combustion reaction has been being used with success for obtainment of several ceramic systems. It is an easy technique, it holds and fast to produce nanosize particles, with excellent control of the purity, chemical homogeneity and with good reproduction possibility of the post in pilot scale (Costa et al., 2007). The use of synthesis methods of ceramic powders that include calcination steps in their synthesis procedure are more appropriate for the development of catalysts for reforming of the methane process. The use of calcination as a heat treatment is very important to remove the carbon waste of the synthesized catalysts. The synthesis method of ceramic powders called polymeric precursor method or Pechini method has proven to be very suitable for the development of catalysts for reforming of the methane process, as the Pechini method includes three steps in its synthesis procedure, the last step being calcination that can be performed at temperatures sufficiently high to cause the volatilization of residual carbon-based substances. Generally, depending on the type of synthesized metal oxide, temperatures values ranging between 500 and 1000° C can be used in calcination. Another advantage of the heat treatment of the Pechini method is that it favors the formation of an atomic structure with high percentage of crystallinity and the formation of size controlled particles. The co-precipitation method is also widely used for the synthesis of catalytic supports for reforming of the methane. Also, this method can synthesize pure or mixed metal oxide. The co-precipitation method is capable of producing metal oxide consisting of particles with controlled sizes, including particles with nanometer dimensions, which play a significant role in various catalytic process. The disadvantage of this method is the existence of multiple steps in the synthesis procedure. However, the metal oxides in the form of ceramic powders can be synthesized by less disseminated methods such as spray dry, freeze dry, sol-gel, hydrothermal method, among others. Regardless the synthesis method used for obtaining a catalytic support formed of metal oxide pure or mixed, in many cases, the active catalytic species is deposited on the support at a later stage of the catalyst synthesis procedure. The active catalytic species can be deposited on the catalytic support by means of different methods. In most cases, in the catalysts for reforming of the methane, the active species are deposited on the catalytic support by the impregnation method also known as humid impregnation method with incipient humidity. In this impregnation method, specific quantities of the catalytic support and of the precursor source of ions of the active catalytic species (usually a metal nitrate) are immersed in aqueous solution. Impregnation is performed by means of rotation followed by drying and calcining to ensure the elimination of the humidity adsorbed in the structure of the catalytic developed material (Figueiredo and Ribeiro, 1987). However, the classic method of preparation of catalysts (humid impregnation) induces carbon condensation (derived from reagent CH<sub>4</sub>) on the exposed crystal of Ni impregnated on the catalyst surface, reducing the catalytic stability and accelerating catalyst deactivation (Leite et al., 2002).

During the impregnation process, after the calcination stage, which is usually performed at a temperature range of 300 - 500°C, this step is concluded and the catalytic system developed is then ready to be forwarded to the catalytic reaction. The temperature value used in the calcination stage of the impregnation process should be selected according to the

material that forms the catalyst system. Factors such as temperature limit before the phase transformations of material structure, type of porosity of atomic structure are assessed here. In order to minimize the coke deposit on the surfaces of catalysts, some alternative methods to suppress the poisoning of the active site metal and the formation of carbon nanotubes are available. Through consecutive reactivation of the catalyst (Ni supported on alumina) with CO<sub>2</sub>-rich atmosphere, it was possible to eliminate the remaining carbon from the catalytic oxidation of the same, with formation of CO (Ito et al., 1999).

The future prospects for the reforming of methane indicate the need for further improvement of this process to optimize its implementation and results. Catalytic systems that are more resistant to coke formation and increasingly appropriate operating conditions of this chemical process will always be the focus of researchers in this area. Certainly, new materials will be produced and tested in the process of reforming of methane, always aiming to reduce the factors leading to deactivation of the catalyst.

The technological innovation in this area may also focus on the discovery or development of new methods for obtaining catalytic systems, in order to ensure the complete mastering of the process of obtaining materials with increasingly controllable physical and structural characteristics. This would lead to the development of catalytic systems more suitable for the reforming of the methane process.

### **5.3. The action of the catalytic system in the reforming of the methane process**

The calcination stage of the impregnation process does not make sure that the active catalytic species of the developed catalytic system have an effective action on the catalytic reaction. So, the active species of the developed catalytic system can only be effectively activated by a heat treatment called Temperature Program Reduction - TPR. This heat treatment is aimed to reducing the active catalytic species deposited in the oxide form on the catalytic support, e.g NiO, in a catalytically active metallic phase, e.g. Ni. This reduction is essential for the occurrence of the catalytic action of the developed material. If the TPR process does not occur, the material developed will be catalytically inert. The treatment of TPR is performed in situ inside of reactor, a few minutes before the catalytic reaction, for example a few minutes before the occurrence of the reforming of methane. In the case of catalytic reactions other than reforming of methane also uses the TPR process to reduce the metal oxide in effectively active species, ie, in metallic phase catalytically active.

In general, at the end of the process of catalytic reforming of methane, the catalyst is recovered and sent for analysis to help characterize this catalyst. The main characteristic to be assessed is the amount of coke deposited on the surface of the catalyst until deactivation. The amount of coke detected on the catalyst system is a function of the type of reforming of methane process accomplished, other factors that influence the formation of coke are the fractions of gaseous reactants injected in the catalytic process input and conditions, e.g. temperature, and especially the type of material that constitutes the catalytic system. Thus, it can be said that the amount of coke detected on the catalyst system characterizes the resistance of this material to the formation of coke. Smaller amounts of coke on the catalyst indicate high resistance to the formation of carbon-based substances.

Finally, it is important to monitor the reforming of the methane process as a whole in order to determine the main factors in this catalytic process, such as the lifetime of the catalyst and the peak values of the temperatures recorded throughout the process. All these combined aspects help define and clarify the success or failure of methane in syngas conversion.

## 6. Conclusion

At the end of this chapter, we believe that we have clarified the importance of a catalytic system (catalyst) in the reforming of the methane process. In fact, the catalyst is an indispensable element in the reforming of the methane process, as well as the subsequent chemical processes that are aimed to obtain high purity hydrogen from syngas, the product of reforming of methane. In the absence of the catalyst, there is no or insufficient interaction between methane and the other reactant (water steam, CO<sub>2</sub> or O<sub>2</sub>). Therefore, we can affirm that the catalyst is an element of the chemical process of reforming of methane which has basically the following functions during the performance of the catalytic process: activate, accelerate, optimize, direct interactions or block interactions. The occurrence of each of these functions depends on the type of reforming of the methane process performed and also on the type of material that constitutes the catalytic system in operation.

Within the operating conditions of reforming of the methane processes, the reagents of these processes interact in gaseous state and in the presence of a catalyst in solid state. Thus, according to the classical definitions of catalysis, the reforming of the methane process is defined as a heterogeneous catalytic process because the reagents and the catalyst interact with distinct phases.

Also, in conclusion of this chapter, we hope that the importance of natural gas in the worldwide energy matrix has become clear. The trend is that natural gas will become even more space in the energy generation area from now on, keeping in view the scarcity of natural resources used as energy generators currently.

Water will remain the most important source of electricity generation worldwide, in the long-term. Nevertheless, it will be hard to construct new hydroelectric dams and reservoirs due to the current policies of environmental preservation. Consequently, alternative forms of energy generation shall be given greater consideration throughout the world.

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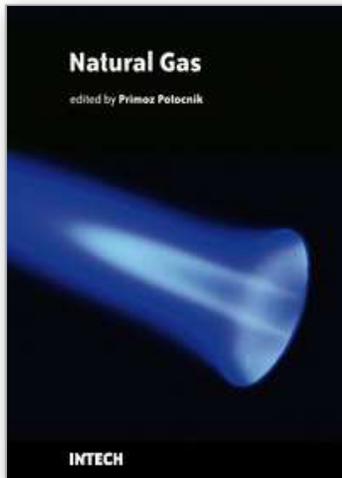
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## Natural Gas

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The contributions in this book present an overview of cutting edge research on natural gas which is a vital component of world's supply of energy. Natural gas is a combustible mixture of hydrocarbon gases, primarily methane but also heavier gaseous hydrocarbons such as ethane, propane and butane. Unlike other fossil fuels, natural gas is clean burning and emits lower levels of potentially harmful by-products into the air. Therefore, it is considered as one of the cleanest, safest, and most useful of all energy sources applied in variety of residential, commercial and industrial fields. The book is organized in 25 chapters that cover various aspects of natural gas research: technology, applications, forecasting, numerical simulations, transport and risk assessment.

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