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Reviews on the Production and Application of Methane

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Abstract: This paper discusses the properties, production and application of methane. It first explains how methane's tetrahedral structure and the slightly polar C-H bond give rise to its physical properties of low melting and boiling point and its chemical properties of oxidation and substitution reaction. It then looks into the three most significant natural and artificial methods to produce methane, including biological decomposition, geological methane generation and methanation. It further identifies methane as a source of clean energy. Compared to traditional fossil fuels such as coal, Methane is more energy efficient and has a much lower carbon emission than traditional fossil fuels such as coal and cruel oil. In terms of using methane as a chemical stock to produce hydrogen, this paper focuses on the chemical mechanism of steam methane reforming (SMR) and methane pyrolysis.

Keywords: Methane, Synthesis, Methanation, Carbon Emission, Methane Pyrolysis.

1. Introduction

In 2003, humans claimed to have discovered a substance in the atmosphere of Mars that indicates biological activities. This substance is methane, which can be obtained by decomposing organic substances [1]. Methane was first discovered by the Italian physicist Alessandro Voltahumans in 1776, who identified the colourless, odourless and flammable gas in Lake Maggiore [2].

Methane is not only evidence for traces of life but also a life-critical liquid for human civilization, just as important as water. Today, methane is not only an essential source of energy worldwide but also an important industrial raw material. Significant amounts of methane are needed for everything from electricity generation, heating, and production of fertilizers and chemicals.

This paper first investigates the chemical structure of methane and then explores some of the well-established production methods and applications of methane.

2. Investigation of Production and Application of Methane

The molecular structure of methane influences its physical and chemical properties to a great extent, which then determines how it is produced and used. As such, this part first analyses the chemical structure of methane and the associated physical and chemical properties. The investigation then goes into some of the most widely adopted production methods of methane. Finally, it ends with a brief look into the usage of methane in the modern economy.

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2.1 Structure and properties

Methane is the simplest alkane. Its chemical formula is CH_4, and its molecular weight is 16.043. As an aliphatic compound, it consists of one carbon atom and four hydrogen atoms and does not contain any functional groups.

2.1.1 *Bonding and Geometry* The carbon atom is bonded to four hydrogen atoms in each methane molecule via single covalent C-H bonds. The C-H single covalent bond is formed by the sharing of two electrons, one from the sp 3 orbitals of the carbon atom and one from the s orbital of the hydrogen atom. The sp 3 orbitals of the carbon are formed by mixing one s orbital with three p orbitals. Hybridization occurs because the s and p orbitals are different in energy, with the s orbital in a lower energy level and the p orbital in a higher energy level. To balance the energy level of electrons and to achieve greater stability, the s and p orbitals merge and equalize in energy level. As a result, each merged orbital, known as the sp 3 orbital, contains 25% characteristics of the s orbital and 75% of the p orbital.

The sp 3 hybridization hybrids also give rise to the tetrahedral structure of methane. The angle between each C-H bond is about 109°. This shape occurs because the negatively charged electron pairs in the C-H covalent bonds repel one another. The tetrahedral structure allows the electron pairs to be far apart [3].

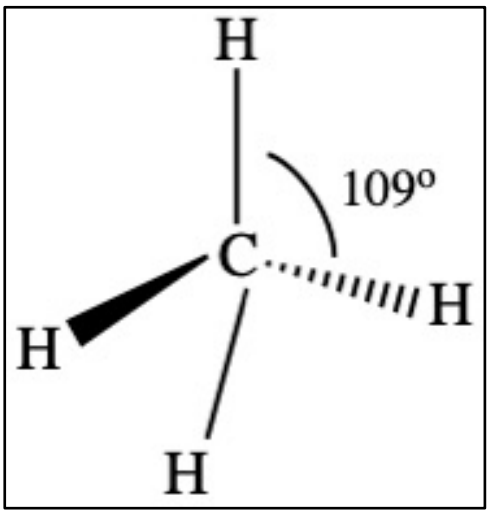


Figure 1. An illustration of the tetrahedral geometry of a methane molecule. Wedge and dash correspond to bonds directed toward and away from the viewer.

2.1.2 Physical properties The C-H bond is slightly polar, and the methane molecule overall is non-polar due to its symmetrical structure. This leads to the weak van der Waals force of attraction between methane molecules and gives rise to the low melting point of −182.5 °C and the low boiling point of −162 °C [3].

2.1.3 Chemical properties The fact that the C-H bond is just slightly polar contributes to its relatively stable structure. The bond pair electrons are shared almost equally by the carbon atom and the hydrogen atoms, making the bond pair a weaker electron donor and thus less susceptible to electron acceptors. The most commonly seen chemical reactions for methane are oxidation and substitution. The oxidation of methane involves the methane and oxygen to form water and carbon dioxide. The reaction equation is shown below:

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O(l)$$

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The substitution reaction of methane involves the hydrogen atoms initially connected to the carbon atom being replaced. One example is chlorination in which the hydrogen atoms are replaced by chlorine atoms. The reaction is a chain reaction which is comprised of three stages. In the first stage, also known as the initiation, the chlorine gas molecule is broken down by UV light into two free radicals. The reaction equation is shown below:

$$Cl_2 \rightarrow 2\ Cl\cdot$$

In the second stage, known as the propagation reaction, the free radicals react with methane to produce intermediates.

$$CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$$
$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

In the third stage, known as the termination reaction, free radicals react with one other and disappear.

$$2Cl\cdot \rightarrow Cl_2$$
$$CH_3\cdot + Cl\cdot \rightarrow CH_3Cl$$
$$CH_3\cdot + CH_3\cdot \rightarrow CH_3CH_3$$

The reaction comes to an end [3].

2.2 Production of methane

Three methods of production of methane are introduced in this part. They are biological decomposition, thermogenic methane generation and chemical synthesis.

2.2.1 *Biological decomposition* A significant amount of methane is generated by the biological decomposition of organic substances. This process is also called methanogenesis. It involves organisms from the domain Archaea undergoing anaerobic respiration [4]. Anaerobic respiration is the metabolism of carbohydrates without the involvement of oxygen. During this process, hydrogen gas and acetic acid are formed [5]. These two substances then go through two different mechanisms to form the final product of methane with the presence of enzymes. The two mechanisms are multi-stage processes, and the net reactions are shown below:

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$
$$CH_3COOH \rightarrow CH_4 + CO_2$$

Water and carbon dioxide are formed as the by-products of the two mechanisms [6].

2.2.2 *Geological methane generation* Geological methane generation contributes to a great deal of methane formation in nature. It involves decomposing organic compounds by the high temperature and pressure in the deep sedimentary strata. It is estimated that the required temperature is within the range of 157° and 221°C. Methane produced by this process is called thermogenic methane. Most of the methane currently extracted by humans from sedimentary basins is thermogenic. Thus, geological methane generation is the most essential method of generating natural gas[7].

2.2.3 *Chemical* synthesis The method to synthesize methane, also known as methanation, was first discovered in 1902 by Sabatier and Senderens. It involves reacting carbon dioxide with hydrogen gas in the presence of a metal catalyst at a high temperature. Methane and water are formed as products.

$$CO_2(g) + 4\ H_2(g) \rightarrow CH_4\ (g) + 2\ H_2O(l)$$

Among many metal catalysts, nickel is the most frequently used because it is relatively cheap and has better selectivity [8].

However, given the abundant naturally occurring methane, the chemical synthesis of methane at the industrial scale seems not to be an economical choice.

2.3 Application of methane

Methane plays an imperative role in modern days. It is a cleaner energy source compared to coal and crude oil, offering heat to factories and households with less carbon emission. It is also the source of hydrogen which can then be used as a chemical feedstock to produce many other chemicals ranging

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from fertilizers to explosives.

2.3.1 Source of clean energy The greenhouse effect has been plaguing the earth's ecology, and methane seems to be a panacea. Natural gas, mostly made from methane, has a substantially lower carbon emission than all other fossil fuels. The study by IEA shows that the carbon emission per unit of energy by natural gas is about 40% less than that by coal and about 20% less than that by crude oil [9].

However, one critic points out the possibility of underestimation of methane emission. Methane is one of the greenhouse gases and can also contribute to the greenhouse effect. The study analyses the past ice cores and showcases that human activities' methane emission has been underestimated by about 25% to 40%[10]. If this is true, methane may not be as clean as a energy source as it is deemed.

2.3.2 Source of hydrogen Steam methane reforming (SMR) is the method of producing hydrogen from methane and is the most cost-effective industrial method. Indeed, more than half of the world's hydrogen is produced using this method [11].

This method is a two-step reaction. In the first step, methane reacts with steam at a high temperature with the presence of the nickel catalyst.

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

In the second step, the intermediate of carbon monoxide reacts further with steam at a lower temperature. An exothermic reaction known as a water-gas shift reaction takes place.

$$CO(g) + H_2O(l) \rightarrow CO_2\,(g) + H_2(g)$$

This reaction has shortcomings since greenhouse gases such as carbon monoxide and carbon dioxide are produced [12].

A cleaner method, methane pyrolysis, is discovered to produce hydrogen gas on a large scale. It enables the production of hydrogen to be zero carbon emission and affordable. This reaction involves melting the metal catalyst and letting methane flow through it. The reaction equation is shown below:

$$CH_4\,(g) \rightarrow C(s) + 2H_2(g)$$

Since carbon produced in this reaction is in the solid state, it does not contribute any carbon emissions into the atmosphere [13].

3. Conclusion

Methane is a treasure to the civilization of the human race. It is plentiful and versatile. It serves as both the source of heat for building and the source of essential chemical feedstock. It will deliver greater potential as a source of clean energy if people can better harness the technology. A study by IEA shows that 75% of methane emission can be eliminated if equipment such as electrical pumps and zero-bleed devices are deployed to capture methane that is leaked during gas operation [14]. Furthermore, solar methane, a device that utilizes a catalyst on the solar panel to produce methane from carbon dioxide, water and sunlight, has achieved substantial progress [15]. Many more exciting scientific discoveries are emerging from the laboratories, and methane can be anticipated to become cleaner soon.

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