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Progress in catalysts of reforming methane process - A potential solution for effective use of CO_2 - rich natural gas sources

Luu Cam Loc, Phan Hong Phuong
University of Technology, VNU - HCM
Email: luucamloc@hcmut.edu.vn

Summary

The rapid increase in emissions of major greenhouse gases such as CO_2 and CH_4 in the last decade has seriously affected the climate change and the living environment in the world in general and in Vietnam in particular. In addition, the demand for effective use of CO_2-rich natural gas has promoted studies to find new, highly active and stable catalysts for the methane reforming process. NiO has proven to be the most suitable catalyst for industrial application of the reforming process. To overcome the disadvantages of NiO-based catalysts such as coke formation and sintering at high reaction temperatures, many diverse researches from using new carriers to supporting catalyst by alkali, alkaline earth metals and other metal oxides to improve the catalyst synthesis method have been conducted. As a result, highly efficient catalysts were created, partly thanks to the reduction of the reaction temperature from 800°C to 700°C, the coke formation significantly decreased and the stable working time of the catalyst increased to over 600 hours.

Key words: CO_2 - rich natural gas, dry reforming, bi-reforming, catalyst.

Introduction

Greenhouse gas emissions causing global warming and climate change has been the issue of concern all over the world. The concentration of CO_2 in the atmosphere increases about 1.5ppm/year in the period 2001 - 2011 [1], 2 ppm/year in the period 2011 - 2015 [2] and it is predicted to reach 661ppm by the end of the 21st century [3]. This led to an increase in the global temperature of 0.8°C in the 20th century and an increase of 1.4 - 5.8°C in the 21st century [4]. CO_2 and CH_4 account for 76% and 16% respectively in total greenhouse gas emission while CH_4 is 21 times more potent to the environment than CO_2 [5]. Currently, the "average mixing ratio" of CH_4 in the troposphere reaches 1.74ppmV, which doubles the pre-industrial period value (0.8ppmV) [6]. For Vietnam, this issue has become more serious and urgent because of rapid industrialisation. According to Vietnam's first report for the United Nations Framework Convention on Climate Change, implemented by the Ministry of Natural Resources and Environment in 2014, in the period 1994 - 2010 total greenhouse gas emissions in Vietnam increased rapidly from 103.8 million metric tons of carbon dioxide equivalent (MMTCDE) to 246.8 MMTCDE. Greenhouse gas emissions in the energy sector increased from 25.6 MMTCDE to 141.1 MMTCDE, making the sector the fastest and the largest emitter in 2010.

In Vietnam, total proven natural gas reserves in 2016 were around 207 billion standard m^3, and marketed production of natural gas was 9,297 million standard m^3 [7]. Besides the qualified reservoirs, some reservoirs with high content of CO_2 have been discovered in recent years. Typically, Lot B - O Mon gas field has a gas capacity of about 107 billion m^3 and the Ca Voi Xanh gas field is estimated at approximately 150 billion m^3, which is 3 times of Lan Tay and Lan Do fields in the Nam Con Son Gas Project [8]. The natural gas extracted from Lot B - O Mon and Ca Voi Xanh gas field contains high amount of CO_2, around 20% and 30%, respectively. In addition, a number of other gas fields also have high concentration of CO_2, such as Song Hong, Phu Khanh, Nam Con Son, Cuu Long, Ma Lay-Tho Chu, and Tu Chinh Region, with proved gas reserves from 2,100 up to 2,800 billion m^3. More specifically, Song Hong field has CO_2 content ranging from 27% to 90% and even 98%. In Ma Lay-Tho Chu basin, CO_2 content is from a little to 80% [8]. The presence of CO_2 with high content in natural gas causes difficulties in exploration and transportation, and that may lead to a huge amount of CO_2 released into the

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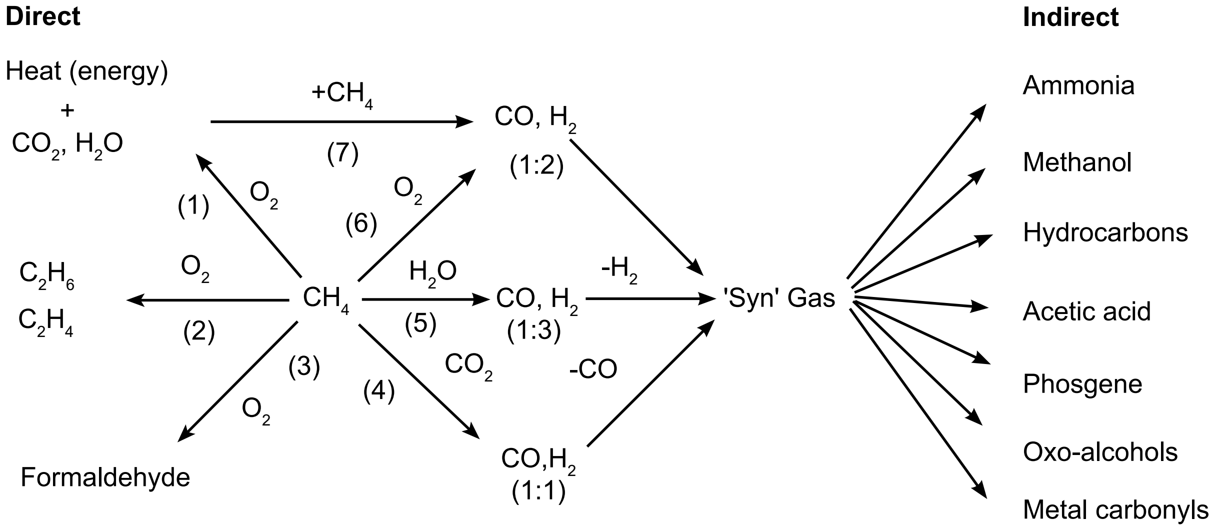

Figure 1. *Various direct and indirect routes for the production of useful chemicals from natural gas [10]*

environment. These facts push the study of processes that convert both CH_4 and CO_2 into final products and/or high-value semi-products such as syngas. These processes not only make use of CO_2-rich natural gas reservoirs effectively but also reduce environmental pollution.

2. Potential utilisation and conversion of CO_2-rich natural gas

Converting CH_4 and CO_2 into high-value products to reduce greenhouse gases and effectively using CO_2-rich natural gas have still been a big challenge because of these highly inactive compounds [9]. However, these two substances can be activated when there are effective catalysts and proper reaction conditions.

It is possible to directly and indirectly convert natural gas into products and semi- products (Figure 1).

Natural gas is used for heating purpose, meanwhile there is a variety of valuable products and semi-products being obtained from syngas, as shown in Figure 1. Today, about 20% of total gas consumption in the world serves energy production (Reaction 1, Figure 1) and this number is estimated to increase sharply in the coming years. In the countries with abundant natural gas resources, power generation accounts for 80% of the gas output. This is because the use of natural gas in energy production causes low environmental pollution, involves low investment cost but brings high thermal efficiency. However, this application direction generates CO_2 emission, which could be converted into syngas in the methane reforming reaction with CO_2 and steam (Reaction 7, Figure 1). Methane can be directly oxidised into formaldehyde (Reaction 3), ethane, and ethylene (Reaction 2). Methane can also be selectively oxidised to syngas by using various oxidising agents in the other three directions (Reactions 4, 5, 6), thereby producing a wide range of chemicals.

Syngas, or synthesis gas, is the mixture comprising of hydrogen, carbon monoxide and very often some carbon dioxide. It has been known for a long time because of its wide range of applications. In the chemical industries, syngas is often used as an intermediate in ammonia, methanol and fertilizers production and to produce its derivatives. Syngas has 50% of the energy density of natural gas, it cannot be burnt directly, but is used as a fuel source. Based on the principle, syngas can be produced from any hydrocarbon feedstock. The conversion of hydrocarbons to hydrogen and syngas will play an important role in the 21st century ranging from large gas to liquid (GTL) plants and hydrogen plants [11]. It is also generated from any other carbon-based feedstock such as petroleum coke, coal, and biomass but the most economical way is from natural gas. Natural gas contains between 70% and 98% of methane, with higher hydrocarbons (ethane to hexane) present in quantities up to a maximum 16%, while diluents (N_2, CO_2) can account for a maximum of 15%, depending on the location from where it is produced [10].

One of the most important applications of syngas in chemical industries is using syngas as feedstocks to produce hydrocarbon and methanol. This reaction is based on the principle of gas-to-liquid theory, and visually it is called Fischer-Tropsch (F-T) synthesis. The F-T chemistry understandably is often regarded as the key technological component of schemes for converting syngas to transportation fuels and other liquid products [12].

Methanol-raw material for the C1 chemistry, thereby producing formaldehyde, acetic acid, chloromethane and other chemicals for the chemical industry, can be produced from syngas or CO_2[13]. In commercial processes for methanol synthesis, methanol has been produced from syngas, which mainly contains CO and H_2 along with a small amount of CO_2[14]. Recently, the synthesis of methanol from carbon dioxide and hydrogen has been intensely studied in connection with the attempts to reduce the emission of CO_2 to the atmosphere. However, the cost of methanol produced by the hydrogenation of CO_2 is higher than the cost of methanol obtained from the CO + CO_2 mixture [15]. Researchers have been trying to improve high performance Cu/ZnO-based catalysts and to develop new catalysts for methanol synthesis from CO_2/H_2 or a CO_2-rich feed ($CO_2/CO/H_2$) [16]. Pilot stage studies of similar projects have already been carried out in Germany [17].

Dimethyl ether (DME) production and Gas to Liquid (GTL) technology are promising processes in using CO_2 as a raw material. There has been a number of technologies using CO_2-rich natural gas for DME and liquid fuel production. DME can be an alternative fuel for LPG and diesel because it has similar properties to LPG and has high cetane number [18]. KOGAS process is the latest generation of DME technology [19]. In this technology, DME is produced from synthesis gas (CO + H_2) through single-phase technology, directly from syngas, or two steps, through methanol synthesis from syngas. However, these technologies have not been adequately studied at commercial scale [19].

Overall, converting CH_4 and CO_2 into synthesis gas for production of other chemicals [20] is a viable way. In the chemical industry, syngas is often used as an intermediate in methanol production, ammonia, Fischer-Tropsch synthesis, production of diesel fuel, fertilizers, derivatives such as acetic acid, gasoline, dimethyl ether and petrochemical synthesis [21]. Synthesis gas is also a source of hydrogen and used in producing aldehyde from olefins.

Syngas production using natural gas

There are 3 main processes to convert methane into syngas, namely steam reforming; dry reforming (CO_2 reforming) and partial oxidation of methane.

Dry reforming of methane (DRM) (1) has drawn attention because this process takes advantage of the available CO_2 in natural gas reservoirs as raw material.

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H = +247\ kJ/mol \qquad (1)$$

Produced synthesis gas at a H_2/CO molar ratio of 1:1 is used in hydroforming to produce polycarbonate or formaldehyde.

Steam reforming of methane (SRM) uses water to gently oxidise methane (2).

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H = +226\ kJ/mol \qquad (2)$$

The main drawbacks of the steam reforming process are high price of steam and formation of large amount of CO_2 in water gas shift reaction (WGS) (3).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41\ kJ/mol \qquad (3)$$

In addition, synthesis gas is obtained with the H_2 to CO ratio of 3:1, suitable for producing ammonia but not for synthesising methanol, acid acetic and hydrocarbon according to Fischer-Tropsch method.

Partial oxidation of methane (POM):

$$CH_4 + ½O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H = -44\ kJ/mol \qquad (4)$$

POM requires the use of pure oxygen and specialised equipment to extract O_2 from the air. Hence, the reforming process proved to be more advantageous.

Dry reforming of methane is strongly endothermic [22] and formation of coke is serious because of high concentration of carbon in feed and there is no oxygen directly involved in gasifying the carbon deposited [23]. Thereby, catalysts lose their activity fast in this dry reforming. Coke is produced from methane cracking reaction (5) and Boudouard reaction (6).

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H = 75\ kJ/mol \qquad (5)$$

$$2CO \rightleftharpoons C_{ads} + CO_2 \quad \Delta H = -86.24\ kJ/mol \qquad (6)$$

To reduce coke deposition, the carbon produced should be consumed in the reverse Boudouard reaction (6). Furthermore, coke formation in reactions (5) and (6) is more favourable at lower temperatures. So, when dry reforming is carried out at below 800°C, carbon is generated from both reactions. At temperatures above 800°C, coke deposited during the dry reforming process originate mainly from methane cracking (5), which is more active than one generated from the Boudouard reaction (6), being easily oxidised by CO_2 present in the reforming reaction [24]. At 700°C, the rate of methane decomposition is higher than the rate of coke oxidation by CO_2. Thus, if a dry reforming process is carried out with high CO_2 to CH_4 ratio (>1) in feed and high temperature, coke formation can be minimised. However, CO_2 to CH_4 ratio is usually approximately equal to 1 to minimise the side reactions such as Boudouard and reverse water gas shift (RWGS), thereby to obtain syngas with a desired H_2 to CO ratio.

Dry reforming process has not been widely applied due to catalytic problems. The catalysts in DRM lose their activity rapidly because of intensive coke formation and metal agglomeration and/or oxidation. Economic efficiency of the use of CH_4 and CO_2 in the industry depends on the energy consumption demand of the reaction. In order to reduce energy costs, it is necessary to lower the reaction temperature. However, from the above analysis, reducing the reaction temperature in DRM to less than 800°C to reduce the energy demand will lead to an increase in coke formation and thereby shorter lifetime of catalysts.

Besides, the suitable molar ratio of H_2/CO for Fischer-Tropsch synthesis is about 2, higher than the one obtained in dry reforming of CH_4 (reaction 1) and lower than the value obtained from methane steam reforming (reaction 2). Combination of dry reforming, steam reforming and partial oxidation of methane (in 3 reactions 1, 2 and 4), called tri-reforming, can solve not only coke formation but also energy demand problems. However, the combination of dry reforming and steam reforming processes (CSCRM), called bi-reforming reaction, is more widely applied to produce syngas [22]. The reaction takes place in the following equation:

$$3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CO + 8H_2 \qquad \Delta H = +220\ kJ/mol \quad (7)$$

CSCRM offers significant benefits over dry reforming, partial oxidation and steam reforming [9]. This combination gives the desired ratio of H_2:CO, perfectly suitable for Fischer-Tropsch synthesis [22] and methanol production [25], and solve the greenhouse gas problem caused by CO_2 generated in steam reforming (3). Moreover, coke formation is restricted by adding steam to the dry reforming feed [26]. In Topsoe technology, the mixture of CH_4, CO_2, H_2O (bi-reforming) is used to reduce coke formation on nickel catalysts and avoid pipe clogging.

3. Catalysts for reforming process

The role of methane reforming has become important along with the development of gas industry. Patents for catalysts in the reforming process increased rapidly over the past two decades (Figure 2).

The reforming process requires high reaction temperatures, up to 800 - 1000° C. Therefore, the catalysts for this process need to have good thermal stability, sintering resistance and high activity [22]. Most of the metals used for reforming methane are noble metals and

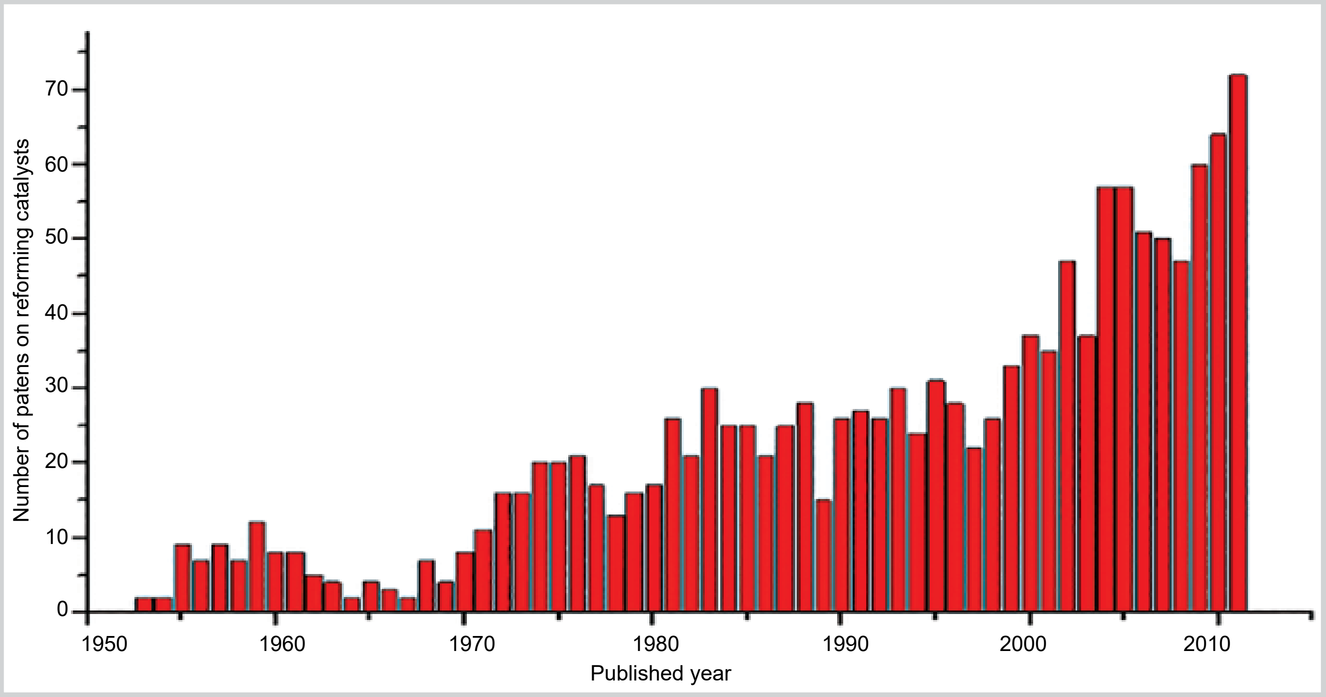

Figure 2. *Patents recorded for reforming catalysts from 1950 to 2010 [27].*

transition metal oxides, which have high reducibility [28]. To meet the mentioned above requirements, the most popular metals used as active phase for the reforming catalysts are Ni, Pt, Ru, Re, Ir, Co, Pd, Rh... [29, 30].

3.1 Noble metal catalysts

Noble metal catalysts have attracted attention because of low coke deposition due to the poor carbon solubility on the surface of these metals [31], high sintering resistance, high stability and activity in reaction at high temperature (>750°C) [32, 33]. Moreover, these metals can be evenly well dispersed on the surface of supports with d electrons, facilitating the adsorption of hydrogen. Some noble metals used as catalysts for reforming are Pt, Pd, Zr, Rh, and Ir [32]. These catalysts are supported on Al_2O_3, MSN or SBA-15. The order of activity of group VIII metals for steam reforming of methane (SRM) is as follows: Rh, Ru> Ni> Ir> Pd, Pt [34, 35]. Rh has the highest activity, followed by Ru. Noble metals are highly active but very expensive. While Ni has quite high activity and cheap. Therefore, nickel based on different supports have been selected to be the commercial catalysts used for methane reforming processes.

3.2. Transition metal catalysts

Although transition metals have lower activity than precious ones, they play an important role in the history of development of catalysts for methane reforming. Transition metals are cheap and available. Most recent studies have focused on VIIIB transition metals except for Os. Especially, Ni, Co and Fe are highly active during CH_4 reforming among others [36, 37]. The activity of transition metals in the dry reforming of methane decreases in the following order: Fe> Ni> Co. Fe-based catalysts give high yield in dry reforming process but poor methane selectivity. High carbon deposittion causes catalyst poisoning and tends to form long chain hydrocarbons and oxygenated compounds on iron-based catalyst. Co-based catalysts are highly active but carbides are easy to form on the surface of catalysts during reaction. Although Ni does not occupy the highest position in the activity range, Ni-based catalysts show high activity and good selectivity while they are cheaper and more available than precious ones [38].

Therefore, commercial catalysts for reforming methane nowadays are mainly high-content metallic Ni dispersed on different supports such as Al_2O_3, MgO, SiO_2, and Cr_2O_3, etc, or mixed oxides [39, 40]. However, the biggest problems of transition metals used as reforming catalysts are coke deposition (especially nickel) and metal sintering [41, 42] resulting in a decrease of catalytic performance. Ni has an affinity for hydrogen that weakens the C-H bond. At high temperature, methane decomposition (5) will occur strongly on active metal sites, forming a carbon layer on the catalysts' surface [43]. Thus, Ni-based catalysts often lose their activity faster than precious metal ones.

The activity and stability of the Ni-based catalysts can be improved by adding promoters, using suitable supports and/or adding agents to oxidise coke such as oxygen or steam into the reaction feed.

3.3. Suports for Ni-based catalysts

The most common support used in the methane reforming process is Al_2O_3. Other supports such as MgO, TiO_2, SiO_2, and La_2O_3 are also used [44]. The order of activity of Ni-based catalysts on the different supports is as follows: Al_2O_3> TiO_2> SiO_2. Effect of the supports is expressed through their influence on direct activation of CH_4 or CO_2 by metal oxides and on the change in the particle size of the metal in the reaction process [45]. Activity of Ni/Al_2O_3 and Ni/SiO_2 catalysts drops with time-on-stream (TOS) in dry reforming of methane because of metal sintering and/or coke formation [46].

After prepared and calcined at 400-600°C, Al_2O_3 surface is partially dehydrated. There exists Lewis basic sites (O^{2-} ion) beside Lewis acidic sites with coordinated holes (Al^{3+} ions) and Bronsted acidic centers (H^+). These Lewis basic sites are capable of adsorption and dissociation of CO_2, an acid gas [47]. However, at reaction temperature of 700-900 °C in the dry reforming, α-Al_2O_3 is more suitable than γ-Al_2O_3 due to thermal stability and high mechanical strength. During the calcination process at high temperature (>1100°C) to form α-Al_2O_3, a part of the Lewis basic sites was lost, leading to an increase in carbon deposition during methane dry reforming.

Nano-sized NiO/α-Al_2O_3 (NiAl) catalysts are successfully prepared by various methods [48-51]. The results show that the catalyst prepared by the impregnation method has the highest activity with 90% of CH_4 and 79% of CO_2 converted at 700°C. This catalyst could maintain its activity more than 30 hours time-on-stream in dry reforming [48-50]. Besides the CH_4 conversion on the NiAl catalyst in the bi-reforming reaction (CSCRM) is higher than the value obtained in dry reforming (95% versus 90%). This is explained by a decline in coke amount produced of about 3.7 times after 30 hours TOS at 700°C, from 37.5 mgC/g-cat in dry reforming to 10 mgC/g-cat in bi-reforming reaction. However, the CO_2 conversion in CSCRM is lower, down to 69% [51]. The reason is that both steam and CO_2 are competitively adsorbed on Lewis basic sites and an amount of CO_2 is produced from steam reforming (reaction 8).

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H = +641\ kJ/mol \qquad (8)$$

Hence, bi-reforming is advantageous over dry reforming in reducing coke production and increasing catalytic stability. Simultaneously, the H_2:CO molar ratio obtained in bi-reforming is approximately 2, suitable for the synthesis of methanol and Fischer-Tropsch process while this ratio in dry reforming is 1, less favourably applied.

S.Wang et al. suggested that the support could improve the activity of Ni-based catalysts [42]. Compared to Ni/Al_2O_3 and Ni/MgO catalysts, Ni/SiO_2 gives higher conversion rates, reaching 96.2% of CH_4 and 93.8% of CO_2 at 800°C. However, these catalysts could not maintain their activity with TOS.

Well-ordered structure silicate materials have been emerging since the early 90s of the 20th century. There are many mesoporous materials synthesised such as FSM, M41S, HMS, MSU-x, SBA-15, and SBA-16, opening a new era in the field of catalysis and adsorption. These materials have uniform pore size (ranging from 20 - 100 Å), being 3 - 4 times wider than pores of zeolite, and large specific surface area (500 - 1000m^2/g). Santa Barbara Amorphous 15 (SBA-15), a mesoporous material owning regular hexagonal pores of 4.6 - 30nm in diameter, has been used as support for NiO-based catalyst in reforming of methane due to its large surface area (600 - 1000m^2/g), high thermal stability, large pore volume (0.5 - 1cm^3/g) and uniform pore size distribution [52, 53]. The replacement of silanol groups on the surface with Ni ions increases the stability of Ni sites on SBA-15.

In our study [54], nanoscale NiO/SBA-15 catalysts with NiO crystallite size in the range of 12.9 to 18.3nm were successfully prepared. In this catalytic system, there are 5 - 6nm NiO particles dispersed inside the pores and the NiO of 20 - 50nm in size distributed on the surface of SBA-15 when NiO content was 30 - 50wt%. Dispersion of metal sites into the pores helps prevent Ni sintering and metal loss during reaction. NiO has such a high dispersion in the catalysts because obtained SBA-15 has uniform pores with large diameters (5.3 - 6nm), high porosity and high specific surface area (613m^2/g). After reduction in H_2, the catalysts have high activity in bi-reforming reaction, reaching 86% CH_4 and 77% CO_2 converted at 700°C or 90.5% and 80%, respectively at 800°C. The catalysts are stable work for hundreds of hours due to presence of weak and strong Lewis basic sites which limit coke formation and increase CO_2 adsorption. Similarly, Zhang et al. [55] reported that 12.5% NiO/SBA-15 catalyst had CH_4 and CO_2 conversion at 800°C of 89% and 85%, respectively and could maintain its activity over 600 hours TOS. As a result, SBA-15 is suitable support for NiO-based catalyst in bi-reforming process. Similarly, interaction between metal-support (Si-O-Ni) in NiO/MSN catalyst helps disperse NiO phase and enhance CH_4 and CO_2 dissociation, leading to an increase in catalytic performance [56].

Recently, many new supports have been reported. For example, metal carbide has been studied as a catalyst because of its unique mechanism. Molybdenum carbide, Mo_2C, has been used as a support for nickel catalysts in the reforming process. CH_4 conversion on this catalyst is nearly 80% while CO_2 conversion can reach up to 100%. However, the lifetime of the catalyst is short (100 - 300 minutes) [57].

Ceria is known as a new generation of support containing lattice oxygen. In addition, CeO_2 can adsorb and desorb H_2O to produce H^+ and OH^- for conversion of carbon on catalysts' surface into CO and CO_2 [58], resulting in a decrease of coke formation.

Our study [59] stated that the physicochemical properties and catalytic activity of NiO catalysts supported on CeO_2 depended on CeO_2 morphology. NiO catalysts supported on CeO_2-nanorod (NR), CeO_2-nanoparticles (NP) and CeO_2-nanocubes (NC) all have high metal dispersion. NiO particles on the first two CeO_2 support are of 5 - 10nm in size while the particles in NiO/CeO_2-NC are smaller and more uniform (5 nm). The high dispersion of NiO in CeO_2 support can be explained by the interaction of Ni^{2+} with CeO_2 forming Ce^{3+} ions and oxygen vacancies, facilitating the formation of Ni-Ce-O solid solution. In addition, NiO/CeO_2 catalysts have 3 types of basic sites giving high CO_2 adsorption capacity. With the outstanding physicochemical characteristics, NiO/CeO_2-NR is more active than NiO/CeO_2-NP and NiO/CeO_2-NC. The CH_4 and CO_2 conversion on NiO/CeO_2-NR in bi-reforming at 700°C are 89% and 67% respectively, while these values are 96% and 72% respectively when the process is carried out at 800°C. Moreover, the amount of coke deposited on this catalyst after 30 hours of TOS at 700°C was very small, 0.54 mgC/g-cat, nearly 20 times lower than the amount of coke obtained on Ni/Al catalyst (10 mgC/g-cat). That is why this catalyst has high stability with TOS in bi-reforming. Other authors [60, 61] also reported that Ni/CeO_2-NR has higher activity and stability than Ni/CeO_2-NP does in dry reforming reaction. This result shows that CeO_2 is a potential support giving high dispersion of active metal, leading to an enhancement of catalytic activity, resistance to coke formation, and an increase of catalysts' lifetime.

3.4. Ni-based catalysts with different promoters

At high reaction temperature, catalysts are unstable and change their structure, leading to metal sintering and coke formation on the catalysts' surface. These cause activity loss of catalyst rapidly [62]. In the NiO-based catalysts, CH_4 adsorbs and dissociates into CH_x intermediate compounds on active metal site (Ni) while support activates CO_2 [63]. In order to reduce the formation of coke, the presence of basic sites is necessary. These sites could be obtained by modifying the supports with alkali metal oxides or rare earth elements. On the other hand, in order to increase selective oxidation activity, promoters such as noble metal or other metal oxide are used to change the NiO reducibility and interaction between NiO and support. This enhancement would result in an increase of NiO dispersion and thereby reduce metal sintering under high temperature of reaction [64, 65].

3.4.1. Alkali and alkaline earth metals

One of the most important factors affecting coke deposition during reaction is the basicity of catalysts [66]. Coke formation can be reduced or even inhibited when the active metal is dispersed on the support as metal oxide with Lewis basic sites. Many studies show that the addition of alkali and alkaline earth metals could change the nature of supports, leading to a reduction of coke formation and an increase of CO_2 adsorption [45]. For example, adding a basic Lewis promoter such as alkali metal oxides (Na_2O, K_2O), alkaline earth (CaO, MgO) or weak base (NH_4OH) reduces coke deposition and metal sintering of Ni/Al_2O_3, Ni/SiO_2 and NiO/SBA-15 catalysts [45, 53, 67].

In Ni/La_2O_3/Al_2O_3 catalyst, the highest yield reaches up to 96% and 97% for CH_4 and CO_2 at 800°C by adding La with a La/Al molar ratio of 0.05 while Ni/CaO/Al_2O_3 catalyst with a Ca/Al molar ratio of almost 0.04 shows the highest efficiency with CH_4 and CO_2 conversion of 91% and 92%, respectively at 800°C [45]. Apart from NiO, reduction of $NiAl_2O_4$ also occurs during extended period of testing resulting in stable activity of the catalyst [68]. The Ni/CaO/Al_2O_3 catalyst shows excellent stability up to 20 hours of TOS at high temperature in the presence of steam, which is mainly due to the high hydrothermal stability of the support.

Z. Hou and T. Yashima [69] and Y.H. Hu [70] agreed that the presence of Mg had decreased the size of Ni particles and increased the dispersion of Ni active sites, hence increased the activity of catalyst and prevented the sintering problem. Furthermore, by adding MgO, the formation of $NiAl_2O_4$ spinel, which is catalytically inactive for methane reforming, had been inhibited.

Our studies in modifying NiO/α-Al_2O_3 and NiO/SBA-15 by MgO [48, 51, 71] showed that strong interaction between NiO with MgO leads to formation of solid solution ($Mg_xNi_{1-x}O$), resulting in a reduction of NiO particle size and sintering of Ni particles. Besides, the presence of Lewis basic sites increases CO_2 adsorption, causing a decrease in coke deposition, thereby increases catalytic activity and stability. CH_4 and CO_2 conversion rates in methane dry reforming at 700°C are 92% and 87% respectively, which are 5% and 9% respectively higher than that on NiAl catalysts. Coke amount obtained after 30 hours TOS on NiO/α-Al_2O_3 promoted by MgO is 7 times lower than on NiAl catalyst (5.25 versus 37.7 mgC/g-cat) [48]. The reduction of coke formation when MgO is added to NiO/α-Al_2O_3 is explained by the presence of MgO or MgO-NiO layers on the catalyst's surface, as shown by TEM image. A similar result is also observed in Ni-MgO/SiO_2 when MgO layer is coated on the catalyst's surface, leading to stable operation in 18 hours of TOS with no coke found [72]. However, MgO does not show a significant effect on NiO/α-Al_2O_3 and NiO/SBA-15 catalysts in bi-reforming, both in terms of activity and coke formation [72]. It has been reported that MgO plays an important role in increasing specific area, metal dispersion and preventing metal sintersing as well as coke formation in Ni/MgO-Al_2O_3 catalyst [73]. Besides, the optimal molar ratio of Mg/Al has been 0.5 because of high Ni dispersion [44]. Our study shows that the optimal ratio of MgO:NiO is 2 and of (NiO+MgO): Al_2O_3 is 0.2 in dry reforming [48].

Alkalisation of NiO/SBA-15 catalyst with NH_4OH could reduce NiO crystallite size down to 10 - 15nm, and increase reducibility and basicity of catalyst. These leads to an enhancement in catalytic activity in bi-reforming of methane [71]. From the above data, MgO is shown to be a promising promoter for NiO-based catalysts in methane reforming because of strong interaction between NiO-MgO which in turn prevents sintering of Ni particles and coke deposition. Besides, alkalisation with ammonia is also an effective treatment for NiO-based catalysts.

3.4.2. Metallic oxide promoters

Besides being used as a support, many studies have proved that CeO_2 is also a superior promoter for NiO-based catalysts in bi-reforming of methane, increasing resistance to coke formation and lifetime of catalysts [49, 74, 75]. The presence of CeO_2 in Ni-Ce/SBA-15 catalyst could remarkably improve activity. The conversion rates of CH_4 and CO_2 on this catalyst are 100% and 90%, respectively [76]. In steam reforming of methane, Ni/CeO_2/SBA-15 catalyst can maintain its activity over 792 hours while CH_4 conversion is 97.5% [77].

Besides CeO_2, precious metals are also used as promoters for NiO-based catalysts in bi-reforming process. The presence of Pt could lower the reduction temperature of NiO. This decrease of reduction temperature can be explained by the spill over phenomenon of hydrogen. Specifically, Pt oxide has a lower reduction temperature than NiO and H atoms generated from dissociative adsorption of H_2 on Pt metal causing an easy reduction of NiO. Therefore, CH_4 conversion is improved [78]. In addition, the presence of Pt could reduce carbon deposition, increase the stability of NiO catalysts and improve the selectivity of H_2 and CO [79]. Rhodium (Rh) is reported to play a similar role as Pt in NiO-based catalysts for methane reforming [80]. Besides the noble metals, Co is also considered a suitable promoter which improves the activity of NiO-based catalyst. Ni-Co/Al_2O_3-MgO catalyst demonstrates enhanced reducibility, owing to strong metal support interaction and thereby high dispersion of metals on support [81]. In dry reforming of methane, the ratio of H_2/CO is nearly 1 on Ni-Co/Al_2O_3-MgO catalyst [82].

ZrO_2 increases dissociative adsorption of CO_2, and reduces $NiAl_2O_4$ formation, resulting in a slight increase in the activity of Ni/Al_2O_3 catalysts in dry reforming of CH_4 [46]. The conversion rates of CH_4 and CO_2 on 10% Ni/Al_2O_3 increase from 67% to 89% and from 70% to 90%, respectively when ZrO_2 is added. Coke formation on this promoted catalyst is also restricted [83].

CuO plays a significant role in stabilising the catalytic structure, preventing the sintering of metal particles. The formation of the Cu-Ni mixture promotes CH_4 dissociation and prevents the increase of carbon fibre on Ni crystals [84]. Addition of vanadium limits the formation of spinel $NiAl_2O_4$ on one hand and improves the catalytic performance in dry reforming of methane on the other hand [85]. Adding V_2O_5 to catalyst NiO/CeO_2-NR could increase CH_4 conversion from 89% to 96% and CO_2 conversion from 67% to 76% at 700°C. After 30 hours TOS, the amount of coke obtained on this promoted catalyst is almost negligible [86]. Hence, NiO/CeO_2-NR has enhanced its catalytic performance when promoted with vanadium.

4. Conclusion

Currently, CO_2 and CH_4 are considered major greenhouse gases that cause climate change, global warming and sea level rise, leading to many catastrophes for humans. However, if there are processes to convert CO_2 and CH_4 into valuable products and/or semi-products, the greenhouse effect will be under control and CO_2-rich natural gas reservoirs will become a source of raw material for the petrochemical industry.

Through conversion of natural gas into syngas, a range of important chemicals can be produced, of which the most important ones are hydrogen, hydrocarbons and methanol. Synthesis gas conversion from natural gas is significantly economic and environmental for Vietnam when there has been an increase in the quantity of natural gas reservoirs containing high concentration of CO_2 found in Viet Nam and some other Asian countries.

The recent trend shows that methane reforming is an effective way for the conversion of CO_2-rich natural gas into syngas. Combination of dry reforming and steam reforming (bi-reforming) simultaneously converts both major greenhouse gases CO_2 and CH_4 into syngas of desired ratio H_2:CO on the one hand and limits the coke deposition due to the presence of steam on the other hand.

Today, nickel is chosen as a highly effective catalyst for methane reforming processes. In the last two decades, there have been many efforts in the development of new catalysts to improve efficiency and save energy in the conversion of CH_4 and CO_2 into syngas. Alkalisation of support, promotion of active phase by promoters as well as adding steam into the reaction medium are effective measures to improve the activity and stability of NiO-based catalysts in methane reforming reaction. There has been a lot of success in using new supports such as CeO_2 and well- ordered mesoporous silica as well as in promoting NiO-based catalysts with alkaline metal or transition metal to reduce coke formation and increase catalytic performance during bi-reforming process. The new catalyst generation can lower the reaction temperature to 700°C while CH_4 conversion reaches up to 97 - 99% and the ratio of H_2:CO is almost 2.

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