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Editors

Prof. Landong Li
Nankai University
School of Materials Science and Engineering
38# Tongyan Road
Haihe Education Park
Jinnan District
300350 Tianjin
China

Prof. Justin S. J. Hargreaves
University of Glasgow
School of Chemistry
Joseph Black Building
G12 8QQ Glasgow
United Kingdom

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Contents

Preface

Energy can be defined as the ability to do work. Specifically, energy exists in various forms such as chemical energy, thermal energy, and radiant energy. Moreover, the controllable transformation of one form to another is of great significance for modern civilization. With the development of human society, the demand for energy has been increasing generally each year, and energy and its interconversion have become a highly topical issue. Nowadays, there are growing concerns not only about accessible energy reserves but also about the energy infrastructure necessary to maintain sustainable development of society. The concept of sustainable energy, which represents energy that can meet current demand and not cause harmful repercussions for the future, is increasingly recognized. Sustainable energy depends upon not only its origin but also how it is utilized.

Catalysis is a process in which a catalyst can change, generally increase, the rate of a chemical reaction without being consumed in the process. It has had huge impact on society, and the rapid development of human society is always accompanied by notable breakthroughs in catalysis, for example, the well-known catalytic ammonia synthesis, catalytic polymerization, and catalytic cracking processes. Catalysis has an indispensable role in industrial production. It is involved in about 90% of chemical processes and the manufacture of over 60% of industrial products.

Catalysis is closely related to energy. In a general catalytic process, a chemical reaction can proceed much faster than that in the absence of a catalyst, and therefore, less energy may be consumed. More intuitively, catalysis can directly participate in the energy transformation processes, for example, converting thermal energy to chemical energy via thermal catalysis, converting photo energy to chemical energy via photocatalysis, and converting electrical energy to chemical energy via electrocatalysis. A key issue in energy transformation is efficiency, and catalysis undoubtedly plays an essential role in promoting the energy efficiency for more sustainable development. It is well known that the energy structure for society is undergoing distinct changes: i.e. the proportion of traditional energy sources like petroleum and coal applied is gradually declining, the proportion of greener energy is gradually increasing, and, correspondingly, the proportion of sustainable energy is gradually increasing. However, society presently must rely on the traditional fossil energy sources of petroleum (~32%), coal (~27%), and natural gas (~24%). Improvements in the transformation of fossil energy or resources via catalysis

can make a significant contribution to modern requirements. On the other hand, the direct generation of sustainable energy from renewable resources via the development of routes involving heterogeneous catalysis might provide a possible solution to the global energy challenges.

Under such circumstances, it is meaningful and desirable to summarize current research progress in heterogeneous catalysis for sustainable energy. Related to this, this book provides a summary relating to the fundamental science of heterogeneous catalysis and sustainable energy, and it is timely to encourage further research activity in this highly topical research field. In this book, two different aspects are summarized, namely, i) the more efficient transformation of fossil resources using heterogeneous catalysis as a tool and ii) the exploitation of renewable energy through heterogeneous catalysis. Specifically, aspects related to hydrogen energy, methane activation, alkane activation, zeolite catalysis, the application of carbon dioxide as building block, and biomass conversion have been included. The authors of the various chapters included in this book are all active researchers in the field of heterogeneous catalysis and sustainable energy. Authors from around the world, including China, the United Kingdom, Australia, Mexico, and Singapore, have contributed.

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By *Landong Li and Justin S. J. Hargreaves*

Part I

Hydrogen Economy

1

Catalytic Hydrogen Production

Xingyuan Gao and Sibudjing Kawi

National University of Singapore, Department of Chemical and Biomolecular Engineering, 4 Engineering Drive 4, 117585 Singapore, Singapore

1.1 Introduction

Currently and in the near future, fossil fuels are/will be the major source of hydrogen production [1, 2]. As shown in Figure 1.1, almost all the industrial manufacturing processes for hydrogen rely on fossil fuels directly or indirectly [1]. Among the fossil fuels like coal, heavy hydrocarbons, and natural gas, methane is mostly studied due to its high abundance in the world, such as in the United States and Malaysia [4–8]. On the other hand, around 48% of hydrogen gas is generated from natural gas [9–11]. Moreover, methane is easy to handle and has a high H/C ratio [12]. Therefore, we focus on the thermocatalytic conversion of methane first in this part, followed by the conversion of other fossil fuels to produce hydrogen gas.

1.1.1 Thermocatalytic Decomposition of Methane

Only hydrogen gas and carbon are produced in the thermal decomposition of hydrocarbons. This CO-free process is promising for industry [13, 14]. As the major component of hydrocarbons, methane has drawn much interest in the recent years in the production of hydrogen gas via thermal decomposition. The reaction mechanisms are shown below [9]. Initially, methane is chemisorbed on the exposed face of catalyst crystals; secondly, C—H bonds are broken in gaseous methane molecules to produce methyl groups and hydrogen atoms, followed by stepwise dissociations to generate CH_x and more hydrogen atoms; thirdly, two hydrogen atoms combine to generate hydrogen molecules, which are released in gaseous form; fourthly, atomic carbon aggregates and diffuses onto the surface of catalyst particles; fifthly, nucleation and growth of carbon filaments occur in the trailing face of catalyst particles.

Among several methane cracking technologies like plasma, pyrolytic, thermocatalytic, and photocatalytic routes, we focus on thermocatalytic decomposition due to the simultaneous formation of carbon nanofibers or carbon nanotubes

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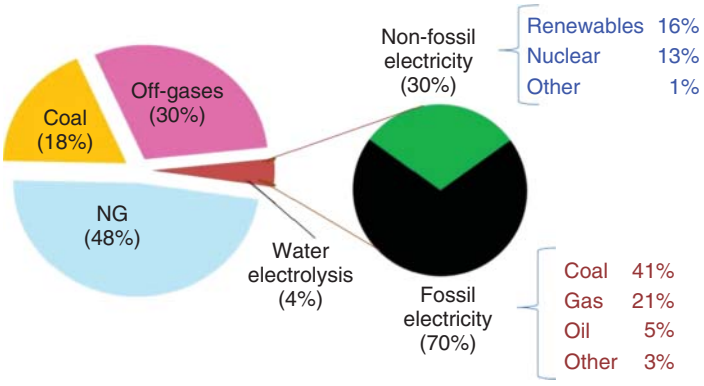

Figure 1.1 The major sources of the industrial hydrogen manufacturing. Source: Reproduced with permission: © 2007, International Energy Agency [3].

that can be potentially used in various applications [14, 15]. Because of the very inactive C—H bond in methane molecules, the activation energy is high, and the reaction is strongly endothermic [16]. Therefore, catalysts are necessary to lower the reaction temperatures and promote the kinetics, including metal- and carbon-based catalysts [1].

1.1.1.1 Metal Catalysts

Since the 1960s, transition metals (Ni, Fe, Co) have been extensively studied and show good catalytic performance in methane decomposition, which occurs at 500–800 °C, much lower than 1200 °C required without a catalyst [17–20]. However, the industrialization of this catalytic system is impeded due to the carbon deposits covering the active sites, leading to rapid deactivation [16, 21]. Modifications have been made to improve the reactivity and stability of transition metal-based catalysts using other transition metals and rare earth metals [22–26].

Bayat et al. [22] studied the Ni–Fe alloy derived from the reduction of the spinel $NiFe_2O_4$ phase. Below 650 °C, the addition of Fe inhibited the encapsulation of carbon by facilitating the carbon diffusion. However, the active sites become fewer with increasing Fe content due to the lower degree of reducibility. To offset the negative effect of Fe, Bayat et al. [23] doped Cu into the Ni–Fe alloy to enhance the methane adsorption and Ni dispersion on alumina. The optimal ratio of Ni/Fe/Cu was 5 : 1 : 1.

Instead of adding Fe, Lua and Wang [24] doped Co into Ni–Cu to form a tri-metallic alloy. Since Co possesses a high melting point, the quasi-liquid phenomenon occurring between 650 and 775 °C was effectively inhibited, leading to enhanced stability. However, phase separation may be an issue with the further addition of Co. Following this work, a series of catalysts comprising Co and W in different ratios were developed [25]. When Co/W equaled 4 : 1, hydrogen gas and multiwall carbon nanotubes were simultaneously produced, showing the highest conversion of methane. It was found that non-interacted Co_3O_4 was responsible for the superior catalytic performance.

Besides doping of transition metals, a series of rare earth metals were added to Ni to form bimetallic catalysts. Among the additives La, Sr, Nd, Pr, Y, and Sm, Ni-La

Table 1.1 Summary of metal catalysts in methane decomposition.

Catalyst	Conditions	Findings	References
Ni–Fe/Al_2O_3	700 °C for 3 h; 30 vol% CH_4 and 70 vol% N_2.	Fe inhibited the encapsulation of carbon by facilitating the carbon diffusion	[22]
Ni–Fe–Cu/Al_2O_3	700 °C for 3 h; 30 vol% CH_4 and 70 vol% N_2.	Cu enhanced methane adsorption and improved the reducibility and nickel dispersion	[23]
Ni–Co–Cu	500–850 °C; 20 vol% CH_4 and 80 vol% N_2.	The high melting point of Co inhibited the quasi-liquid phenomenon, leading to an enhanced stability	[24]
Co–W/MgO	700 °C; CH_4 at a flow rate of 50 sccm.	When Co/W equaled to 4 : 1; non-interacted Co_3O_4 was responsible for the highest conversion of methane	[25]
Ni–La–Si	300∼750 °C; CH_4 at a flow rate of 10 ml min^{-1}	The high activity and low solid carbon formation were attributed to the good thermal stability and small Ni particle size	[26]

exhibited the highest activity and lowest solid carbon formation due to their good thermal stability and small Ni particle size [26] (Table 1.1).

1.1.1.2 Carbon Catalysts

Due to the low cost, resistance to sulfur, and temperature, various carbon materials have been studied as alternatives to transition metals in methane decomposition [1, 16], including active carbon particles [27–30], ordered mesoporous carbons [31, 32], carbon black particles [33], and commercial carbon materials [34]. However, gradual deactivation occurred on carbon catalysts resulting from the coverage of inactive turbostratic carbon. To alleviate this issue, Muradov et al. [35] prolonged methane decomposition by generating active carbon aerosols continuously in a non-thermal plasma device. Besides, Dufour et al. [36] discovered that the addition of small amounts of oxidizing agents like oxygen, CO_2, and steam in the feedstock could effectively enhance the sustainability. Furthermore, the gaseous form of carbon particles derived from partial gasification could inhibit the deactivation of catalyst in a fluid state and cyclic process between the reactor and heater [37].

1.1.2 Partial Oxidation of Methane

Partial oxidation of methane (POM) has drawn much attention recently due to the compactness, good response time, and lower sensitivity to the type of fuels. In the

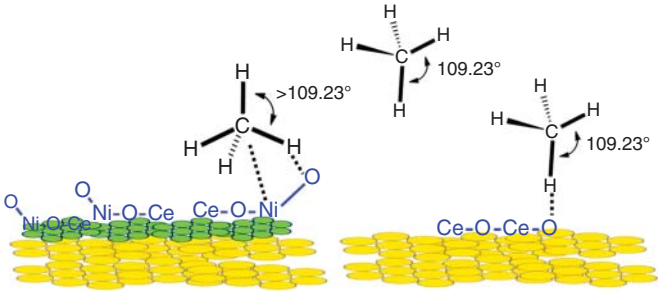

Figure 1.2 Schematic representation of Ni/CeO_2 and CeO_2 surface having surface defects with under coordinated oxygen atoms. Source: Reproduced with permission from Pal et al. [40]; © 2015, American Chemical Society.

presence of oxygen, POM is considered as a fast and highly exothermic reaction to produce syngas as shown in Eq. (1.1) [38]:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H^{\circ}_{298\ K} = -35.6\ \text{kJ mol}^{-1} \tag{1.1}$$

The reaction can occur at a very high temperature without catalysts. However, the use of catalysts can lower the reaction temperature greatly that saves the energy input. The commonly studied catalysts for POM include transition metals, noble metals, and perovskites as shown in Table 1.2.

Amongst the transition metals, Ni with different supports is widely applied in POM. Pantaleo et al. [39] compared the catalytic performance of CeO_2 and La_2O_3 single oxide supports and CeO_2–La_2O_3 mixed oxide supports prepared by wet impregnation and coprecipitation. Interestingly, coke only deposited on the single oxide supported catalysts. The enhanced anti-coking property of mixed oxide supported catalyst was attributed to the formation of a series of Ni–La_2O_3 species with different oxidation states of Ni. Besides, in another study regarding Ni/CeO_2 [40], the surface and point defects with undercoordinated oxygen atoms in CeO_2 originating from the formation of O–Ni–O–Ce superstructures promoted the activation of C—H bonds (Figure 1.2). In addition to Ni-based catalysts, Co/ZrO_2 exhibited a very high conversion of methane and selectivity to hydrogen gas, out-performing many other catalysts [41].

Noble metals are also used in POM. A comparison among Pt, Pd, and bimetallic catalysts was conducted by Abbasi et al. [42]. It was found that Pd performed the best in this comparison, followed by the mixture and Pt alone. On the other hand, supports can also affect the performance of Rh-based catalysts [43]. Due to the oxygen spillover from $Ce_{0.5}Zr_{0.5}O_2$, Rh was easily reoxidized and lost active sites; however, this spillover effect could be alleviated by Al_2O_3.

Perovskite structures present superior anti-coking properties due to the reaction of carbon deposits and oxygen species derived from the structure [60]. $Sr_{0.8}Ni_{0.2}ZrO_3$ exhibited a highly stable conversion of methane at 900 °C under a reducing atmosphere [44]. Similarly, $LaGa_{0.65}Mg_{0.15}Ni_{0.2}O_3$ achieved 81% conversion of methane and 100% selectivity to hydrogen gas at 900 °C. This excellent catalytic property may be attributed to the existence of La_2O_3 and $La_2O_2CO_3$ besides the perovskite structure [45].

Table 1.2 Summary of catalysts in partial oxidation of methane.

Catalyst	Conditions	Findings	References.
$Ni/CeO_2–La_2O_3$	700 °C; WHSV = 60 000; O/C = 0.5	Over 90% methane conversion; the formation of a series of $Ni–La_2O_3$ species with different oxidation states of Ni inhibited cokes	[39]
Ni/CeO_2	750 °C; WHSV = 50 000; O/C = 0.5	Over 85% methane conversion and 65% H_2 selectivity; the surface and point defects originated from the formation of O–Ni–O–Ce structures activated the C—H bonds	[40]
Co/ZrO_2	800 °C; WHSV = 60 000; O/C = 0.5	Co/ZrO_2 exhibited 100% conversion of methane and 98.1% selectivity to hydrogen gas	[41]
$Pd/\gamma\text{-}Al_2O_3$	650 °C; WHSV = 38 400; O/C = 2	Pd performed the best (nearly 100%), followed by Pt–Pd and Pt alone	[42]
Rh/Al_2O_3 and $Rh/Ce_{0.5}Zr_{0.5}O_2$	600 °C; WHSV = 252 000; O/C = 2	Rh was easily reoxidized by oxygen spillover in $Ce_{0.5}Zr_{0.5}O_2$; this spillover effect could be alleviated by Al_2O_3, maintaining 60% methane conversion for 10 h	[43]
$Sr_{0.8}Ni_{0.2}ZrO_3$	900 °C; WHSV = 66 000; O/C = 0.5	Over 94% methane conversion; a highly stable conversion of methane at 900 °C under reducing environment	[44]
$LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-\delta}$	900 °C; WHSV = 3300; O/C = 0.5	81.2% methane conversion and 100% H_2 selectivity were attributed to the existence of La_2O_3 and $La_2O_2CO_3$ besides the perovskite structure	[45]
$Pt–NiO/Al_2O_3$	800 °C; WHSV = 7200; O/C = 0.5	91.8% methane conversion and 98.4% H_2 selectivity; Ni reduction was promoted by Pt	[46]
Co/Al_2O_3	850 °C; WHSV = 60 000; O/C = 0.5	95% methane conversion and 93.6% H_2 selectivity were attributed to the formation of Co_3O_4 as the major phase after 500 °C calcination	[47]
$Ni/12CaO{\cdot}7Al_2O_3$	800 °C; WHSV = 30 000; O/C = 0.5	Over 90% methane conversion and 95% H_2 selectivity were attributed to the active oxygen ions and high dispersion of Ni.	[48]

Table 1.2 (Continued)

Catalyst	Conditions	Findings	References.
Co/MgO	850 °C; WHSV = 20 000; O/C = 0.5	95% methane conversion, little coke formation, and sintering were attributed to small crystals embedded in the support derived from CoO–MgO solid solution	[49]
$Ni/CeO_2/Al_2O_3$	800 °C; WHSV = 152 432; O/C = 0.5	Low loading of CeO_2 (1%) generated a highly dispersed CeO_2 particle, enhancing the reducibility and obtaining 80.3% methane conversion with less carbon deposition	[50]
$Ni–Cr/Al_2O_3$	700 °C; WHSV = 195 000; O/C = 0.5	85% methane conversion and enhanced stability were realized by the more dispersed Ni particles and surface basicity with addition of Cr	[51]
$Ni–Rh/Al_2O_3–MgO$	750 °C; WHSV = 354 044; O/C = 0.5	93% methane conversion and 95% H_2 selectivity; Rh prevented the oxidation of Ni	[52]
Rh/CeO_2	700 °C; WHSV = 60 000; O/C = 0.5	The Rh ions in the surface lattice of CeO_2 were active in POM and obtained 95.2% methane conversion and 92.9% H_2 selectivity	[53]
$Ni/ZrO_2@SiO_2$ core shell	750 °C; WHSV = 50 000; O/C = 0.5	Over 90% methane conversion and 75% H_2 selectivity were obtained with strong coke resistance due to the high oxygen storage capacity and steric hindrance	[54]
Ni/zeolite catalysts	750 °C; WHSV = 90 000; O/C = 0.5	100% methane conversion with strong anti-deactivation ability was attributed to less surface acidity and higher thermal stability	[55]
Ni/TiO_2	800 °C; WHSV = 4800; O/C = 0.5	86.3% methane conversion and 99.7% H_2 selectivity were obtained, but serious deactivation was observed, resulting from the NiO and $NiTiO_3$ formation	[56]
$LaCoO_3/\gamma\text{-}Al_2O_3$	800 °C; WHSV = 899 550; O/C = 0.25	Over 35% methane conversion and 40% H_2 selectivity; excellent stability was caused by highly dispersed Co and carbon removal by La_2O_3	[57]

Table 1.2 (Continued)

Catalyst	Conditions	Findings	References.
$La_{0.08}Sr_{0.92}Fe_{0.20}Ti_{0.80}O_3$	900 °C; WHSV = 30 000; O/C = 0.5	Over 50% methane conversion and 60% H_2 selectivity; high oxygen vacancy concentration was responsible for the high activity	[58]
$La_{0.5}Sr_{0.5}CoO_3$	850 °C; WHSV = 30 000; O/C = 0.5	Over 70% methane conversion and 75% H_2 selectivity were realized with highly dispersed Co particles in the La_2O_3 and SrO matrix	[59]

WHSV, weight hour space velocity (unit: ml h^{-1} $g_{cat}{}^{-1}$); O/C, O_2-to-carbon ratio.

1.1.3 Catalytic Reforming of Methane

The popular syngas production methods consist of steam reforming of methane (SRM), oxidative steam reforming of methane (OSRM), and dry reforming of methane (DRM). The following will respectively introduce the reaction mechanism, issues to be overcome, and catalytic systems. Kinetic modeling will also be included.

1.1.3.1 Steam Reforming of Methane (SRM)

SRM possesses many advantages, including high hydrogen yield and low cost to obtain hydrogen gas [61, 62]. The reaction equation is shown as below:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^{\circ}_{298\ K} = 206.2\ kJ\ mol^{-1} \tag{1.2}$$

Due to the endothermic nature of this reaction, a high reaction temperature is preferred to generate a high yield of H_2 [63]. However, a simultaneous water–gas shift (WGS) reaction occurs, and the CO conversion is inhibited at high temperatures since WGS reaction is exothermic according to Eq. (1.3) [64]:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298\ K} = -41\ kJ\ mol^{-1} \tag{1.3}$$

To solve this issue in industry, a two-reactor system has been adopted to achieve both a high conversion of methane and a high yield of H_2. In detail, the reactants, methane and steam, are passed through the first reactor operated at 300–450 °C where the reaction is accelerated kinetically and more methane is converted thermodynamically according to Eq. (1.2) in spite of the low conversion of CO according to Eq. (1.3). Afterward, the intermediate products are continuously fed to the second low-temperature reactor (175–250 °C) with a high ratio of steam to convert more CO to form CO_2 and H_2 [65, 66].

To further purify or enhance the yield of hydrogen gas in the final products, CO_2 and H_2 is required to be removed *in situ* respectively by sorbents and selective membranes as shown in Figure 1.3 [67].

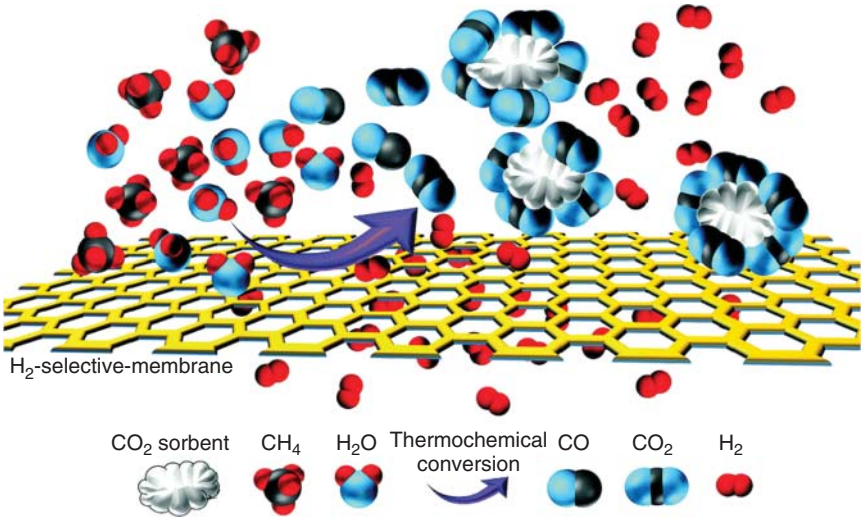

Figure 1.3 Representation of H_2 and CO_2 removal by H_2-selective membranes and using CO_2 sorbents. Source: Reproduced with permission from Ji et al. [67]: © 2018, The Royal Society of Chemistry.

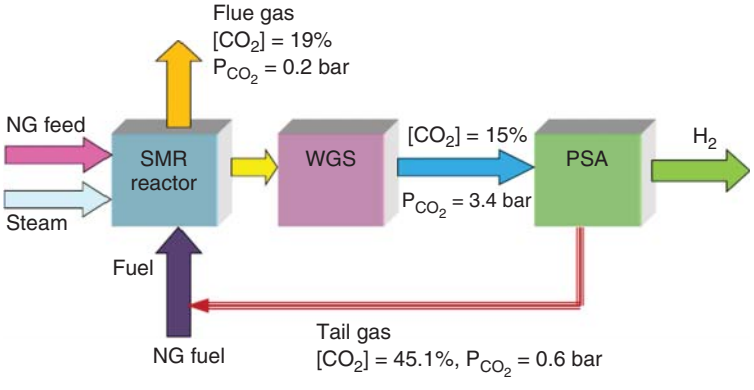

Figure 1.4 Simplified block diagram of a modern SMR plant with major CO_2 containing streams. SMR, steam methane reforming; WGS, water–gas shift reactor; PSA, pressure swing adsorption unit. Source: Reproduced with permission from Muradov [1]: © 2017, Elsevier.

Specifically for CO_2 sorbents, different from the hot potassium carbonate or amine scrubber used about two to three decades ago, pressure swing adsorption (PSA), a physical adsorption technology, is widely adopted in modern SRM plants, achieving an ultrahigh purity of 99.999% for H_2 (shown in Figure 1.4) [1]. In this process, CO_2 is not selectively separated from other gases, but used together with CH_4 and CO to provide heat for the reformer with CO_2 as an exhaust vented out of the reactor system in the end [68].

Besides the design of the reactor system, SRM catalysts should possess the follow stringent features: high catalytic stability, high conversion of methane, superior