Catalytic Methane Combustion in Microreactors

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Chapter 6

Catalytic methane combustion: conclusions, challenges and future prospects

In this chapter, the main findings of this thesis have been firstly summarized. Then, the challenges and future prospects have been proposed for the catalytic methane combustion (CMC) in microreactors.

6.1. Summary of the current thesis

The main conclusions in this work are summarized as follows.

In Chapter 2, a comprehensive literature review of CMC has been presented, including the different catalyst types, reaction mechanisms and kinetics, reaction conditions (e.g., the effect of temperature, space velocity, oxygen to methane molar ratio, natural gas composition, operating pressure) and various applied reactors (e.g., fix-bed, wall-coated, membrane, fluidized bed), which offers a comprehensive reference for the follow-up research in this field.

In Chapter 3, the stability and adhesion of washcoated $Pt/\gamma\text{-}Al_2O_3$ catalyst has been examined in a multichannel microreactor. A best adhesion of $\gamma\text{-}Al_2O_3$ layer could be obtained by choosing the suitable binder (e.g., PVA with 3 - 5 wt% and MW of 57,000 - 186,000), initial $\gamma\text{-}Al_2O_3$ particle size (3 μm) and pH value (pH $\approx$ 3.5), in order to form the sufficient hydrogen bridges with the well-dispersed alumina. Furthermore, the FeCrAlloy used as the microreactor substrate presented a better adhesion both for rectangular and round channels than 316L stainless steel. The washcoated $Pt/\gamma\text{-}Al_2O_3$ catalyst was further realized in the parallelized multichannel microreactor for CMC tests following the above identified optimized coating procedure. It has been found that the operating temperature has the greater influence on the methane conversion compared with those of the gas flow rate and O_2/CH_4 molar ratio. The favourable coverage of the adsorbed methane and oxygen over the catalyst surface is essential to obtain a desired methane conversion. Moreover, more reaction heat was released from the reaction at a higher flow rate, causing an obvious temperature increase along the microreactor. Similarly, the microreactor temperature was increased with increasing O_2/CH_4 molar ratio. The temperature profile along the multi-channel microreactor is in line with the methane conversion obtained therein.

In Chapter 4, the CMC was performed in the single-layer and multi-layer washcoated $Pt/\gamma\text{-}Al_2O_3$ catalysts deposited inside the capillary microreactors. Two different cases were tested in the multi-layer system. In case 1, the total weight of Pt in the catalyst in the multi-layer system was maintained theoretically the same as that the single-layer system. In case 2, the theoretical Pt loading in the multi-layer system was kept identical to the respective single layer system. The coating thickness in both cases could be assumed to increase proportionally with the number

of layers. The influences of operating conditions (e.g., the reaction temperature, molar ratio of oxygen to methane and total flow rate) as well as the Pt weight and loading were examined. In the single-layer catalyst system, a best methane conversion of 95.17% could be obtained under 500 °C at a total flow rate of 30 mL min^{-1} and an oxygen to methane molar ratio (Φ) = 2. The methane conversion exhibited a remarkable increase with the increasing Pt loading or mass, and the light-off phenomenon started to occur at above 400 °C. The difference in the increment of the methane conversion tended to slow down with the Pt loading increase, possibly caused by the more significant internal diffusion limitation in the coating given the increased intrinsic kinetic rate. A lower methane conversion was obtained at Φ = 5 than that at Φ = 2 in the light-off experiment due to the competitive adsorption of the reactants. The decrease in the methane conversion tend to slow down at sufficiently high flow rates, which could be attributed to the improved external mass transfer that compensated the decreased conversion therein. In the multi-layer system in case 1, the double-layer catalyst system yielded a lower methane conversion at Φ =2 and 5 than that of the corresponding single-layer system at otherwise identical working conditions. This is possibly caused by the more significant internal diffusion resistance in thicker coating layers. When it comes to case 2, the double- and triple-layer catalyst systems generally yielded a higher methane conversion at Φ =2 and 5 than that of the respective single-layer system, indicating the (active) participation of all coating layers (instead of the top layer alone) in the reaction. Another implication is that in case 2, the reaction rate tended to be more limited by the catalyst amount than the internal diffusion. However, the methane conversion is nearly identical between the single-layer and the double- and triple-layer (case 2) systems at Φ = 1 throughout the studied temperature range (350 - 500 °C), because the reaction rate is mainly limited by the insufficient oxygen supply.

In Chapter 5, the straight parallel channel microreactor (Reactor #1) deposited with Pt/γ-Al$_2$O$_3$ catalyst was firstly examined for the CMC. The optimized specific catalyst loading of 57.6 g m^{-2} presented a best methane conversion. An obvious decrease in the methane conversion with higher or lower specific catalyst loadings could be explained by the increased internal diffusion resistance in thicker coatings or and the absence of sufficient active sites in thinner coatings, respectively. A higher methane conversion could be obtained when using the tree-like structure as the outlet product collector rather than as the inlet fluid distributor, especially at high flow rates. This could be explained by the higher local at the inlet and outlet of the reaction microchannel, which is beneficial for a more uniform fluid distribution therein. Subsequently, the CMC has been performed in other plate-type microreactors with various internal channel

configurations coated with Pt/γ-Al$_2$O$_3$ catalyst, including cavity microreactor (Reactor #2), double serpentine channel microreactor (Reactor #3), obstacled straight channel microreactor (Reactor #4), meshed circuit microreactor (Reactor #5) and vascular microreactor (Reactor #6). The double serpentine channel microreactor has shown the highest methane conversion, which could be due to the proper coverage of the coating surface area and a relatively long residence time. Moreover, an improved gaseous mixing in the serpentine microchannels could resulted in an improved external mass transfer and thus contributed to a higher methane conversion. On the contrary, the meshed circuit microreactor presented the lowest methane conversion, probably due to the divergent flow presented in the flow circuit. This probably resulted in a non-uniform flow distribution and/or somewhat broader residence time distribution, and thus the lowest methane conversion. The results regarding the influence of the reaction temperature, molar ratio of O$_2$:CH$_4$ and total flow rate in these microreactors are generally in line with those observed in Chapter 4.

6.2. Short-term research work as a continuation of the current thesis

Although a substantial research effort has been elaborated in this thesis, the investigations are still far from being over, especially on the improved catalyst activity, the understanding of the catalytic behaviour between active sites and the adsorbed reactants, the reaction pathways, and ways to suppresses the catalyst deactivation. Possible extensions of the current thesis are briefly summarized as follows.

6.2.1. Noble metal catalyst

In the current thesis, the monometallic Pt/γ-Al$_2$O$_3$ catalyst has been used for the CMC. The improvement of catalyst activity (e.g., using different active species and supports) has not been addressed. In this regard, the bimetallic catalysts (e.g., Pt-Pd [1,2], Pd-Ce [3,4], Pt-Co [5]) could be selected as a priority for the following research work. Bimetallic catalysts present many advantages over monometallic catalysts [6-8], because of the presence of a better synergetic effect between the metal-metal interactions [9,10]. Moreover, the introduction of Pt into Pd-based catalyst is beneficial to increase the dispersion of active sites [11], thermostability [12] and the oxygen exchange [13]. The increased cost is their main disadvantage. More efforts should be paid on combining non-noble or transitional metals (e.g., Fe, Ni, Mg, Co) with noble metal catalysts (e.g., Pt, Pd), which could ensure the high catalytic activity at a reasonable cost of catalysts.

In addition to the active species mentioned above, the catalyst support also plays an important

role. In our thesis, γ-Al$_2$O$_3$ has been used exclusively as the support, due to its high chemical stability and mechanical resistance. However, surface properties of γ-Al$_2$O$_3$ might be changed at the high temperature levels, which could result in the reduced specific surface area and thereby lower catalyst activity. ZrO$_2$, CeO$_2$, MgO, SiO$_2$, zeolites and other non-noble metal oxides with improved thermal stability may be considered as the support for the next stage. It is reported that the introduction of CeO$_2$ as support effectively promoted the oxygen species exchange between the active composition and support [14,15]. The addition of ZrO$_2$ in PdO/Al$_2$O$_3$ catalyst exhibited a better active site reformation, resulting in a higher methane conversion [16]. Moreover, the support properties (e.g., basicity/acidity, electrophilic/electrophobic properties) could directly affect the oxidation state of the active species, which in turn determines the catalytic activity. Yoshida et al. [17] reported that Pd/MgO and Pd/ZrO$_2$ catalyst with lower acidity presented a decrease in the methane conversion despite the higher Pd oxidation state on MgO and ZrO$_2$. The highest methane conversion can be found for Pd/Al$_2$O$_3$ and Pd/SiO$_2$ catalyst due to the use of higher acidic supports. When the acidity continued to increase, SiO$_2$-ZrO$_2$, SiO$_2$-Al$_2$O$_3$ catalysts rendered a decrease in the methane conversion as a result of lower Pd oxidation state from the strong acidic support [17]. Additionally, the binary oxide could be formed between the support and the active species (e.g., PdO-MgO) so as to stabilize the cluster anion by electrooptic cations.

Based on the discussion above, more promising attempts could include (but is not limited to) Pt-Mg, Pt-Ni, Pt-Fe as active species, and ZrO$_2$, CeO$_2$, SiO$_2$, TiO$_2$ as support. Other substituted additives (e.g., La, Mn, V, Ba, etc.) may also be considered to further adjust the catalyst acid/base strength, the interaction strength between active species and support, and the increase of oxygen vacancies.

6.2.2. Coating preparation

In current thesis, Pt/γ-Al$_2$O$_3$ catalyst has been successfully coated onto the microreactor wall by using the suspension method (i.e., the slurry coating technique). This method needs to be experimentally adjusted once varying active species and supports, i.e., for various bimetallic catalysts (e.g., Pt-Mg, Pt-Ni, Pt-Fe as active species, and ZrO$_2$, CeO$_2$, SiO$_2$, TiO$_2$ as support). Other preparation methods need to be attempted in order to ensure the adaptability for certain washcoat catalysts, as referred to elsewhere (e.g., a dip-coating [18], sol-gel [19,20], chemical vapor deposition [21,22], physical vapor deposition [23,24]).

In the thesis, Pt/γ-Al$_2$O$_3$ coating catalyst has been studied in round tube made of stainless steel.

The adhesion properties have been found to still have space for improvement (Chapter 2). The introduction of Fe_2O_3, NiO, Cr_2O_3 into $Pt/\gamma-Al_2O_3$ coating catalyst may help, owing to the possible formation of chemical bonding between catalyst and stainless steel. The main composition of stainless steel (e.g., Fe, Ni, Cr) might have more affinity with the catalyst containing those species, and thus further verification is needed. Meanwhile, it is strongly suggested to test the recycling of washcoat catalyst in the stainless steel microreactor, and to compare the fresh and the re-used washcoat catalyst regarding the catalytic performance in future studies.

Additionally, as for the bimetallic catalyst preparation, it is worth noting that different structures (e.g., core-shell [25,26], alloy [27], heterostructure [28]) could be adjusted by employing different preparation methods, resulting in the significant difference on the catalyst activity [29]. Among different structures, Pt-Pd alloy can be easily formed during the calcination step by traditional impregnation methods [30], leading to the improved catalytic activity [30,31]. However, other studies illustrated that the formation of Pt-Pd alloy structure presented a negative influence on the methane conversion [32,33]. This different point of view might be due to different procedures during the catalyst preparation, or the different reaction conditions triggered [34]. The property of single Pt and Pd particles might be deprived after the formation of Pt-Pd alloy. Therefore, the development of bimetallic catalysts with a precise control of the target structure is still a challenge by far.

6.2.3. Catalyst deactivation

In Chapters 3 and 4, the catalyst life of $Pt/\gamma-Al_2O_3$ has been examined in the fixed-bed reactor or microreactor for up to 100 h, and the catalyst activity presented an obvious decrease at increasing reaction time in our experiment. Herein, the catalyst deactivation is another important issue to be addressed to prolong the catalyst life for its wider application in practice [35]. By overviewing catalyst deactivation causes and mechanisms [36,37], three fundamental reasons can be generally summarized: poisoning, coking or fouling, and ageing. The coke deposition is carried out by blocking active sites, whereas catalyst aging is commonly caused by sintering that refers to the reduction of specific surface area, and eventually result in the structure modification and catalyst deactivation. Meanwhile, the catalyst poisoning could be also caused by the strong chemisorption on the active sites from the impurities (e.g., sulfur, chlorine) included in the reactant gases, resulting in the alteration of active sites and irreversible deactivation of catalyst [37].

More attempts thereby are proposed to deal with the catalyst deactivation in the future research.

(1) As for Pd-based catalysts, at least both the dispersed and crystalline PdO phases are commonly considered as active sites existing on Al_2O_3 support, as reported by Farrauto et al. [16]. Owing to the highly exothermic reaction, the actual temperature inside the catalyst could be extremely high (adiabatic temperature rise is equal to ca. 2000 ^oC at Φ = 2). It results in the growth of Pt particles and the formation of less active PtO_2 [38,39], which will possibly accelerate the catalyst deactivation [40]. The addition of promoters (rare earth oxides) into the catalysts could be alternative solutions to resist deactivation by increasing the thermal decomposition temperature[16]. Additionally, the use of bi-/triple-metallic catalysts may also dramatically prevent the catalyst deactivation [41].

(2) The reversible deactivation of catalyst caused by water vapor and CO_2 could be attribute to the formation of hydroxyl group over the catalyst surface, hindering the exchange of oxygen species [42,43]. Further experimental work on preparing new supports and/or additives to suppress the formation of hydroxide is highly recommended in order to enhance the oxygen mobility.

(3) One of the highly challenging issues is to develop catalyst with the excellent resistance to the sulfur poisoning. The noble-metal catalyst could be easily poisoned when exposed to the natural gas containing sulfur compounds (e.g. SO_2/H_2S) [44,45]. The mechanism of Pd-based catalyst deactivation by sulphur poisoning has been established by many researchers [35,44,45]. The formation of the inactive stable sulphate species ($PdSO_3/PdSO_4$) results in the irreversible deactivation of the catalyst, and the capacity of SO_2 adsorption plays an important role in the sulfur resistance [46]. Thus, it is essential to develop the noble metal-based catalysts with high resistance to sulphur species which are able to dramatically decrease the stability of Pd sulphate species over the catalyst surface.

(4) The catalyst regeneration is an essential strategy to effectively reuse catalysts after deactivation. It has been reported that sulfur-poisoned Pd-based could be regenerated under H_2 or He atmosphere, somehow removing the sulfur species from the catalyst surface [47]. Overall, the comprehensive understanding of the regeneration mechanism and kinetics is not much reported. More effective procedures and methods for the catalyst regeneration are still needed by far.

As for this thesis, the recycling of washcoat catalyst needs further investigation on the stainless steel microreactor. It would be interesting to characterize the catalyst recovery efficiency and

the catalyst activity after certain rounds of recycling experiment.

(5) Possible pretreatment on desulfurization of natural gas still needs to be improved in order to better satisfy the downstream reactions. Concerning the pollutant regulations, more investigation should be invested on biomethane in the future, which is a green alternative path with low emission compared with convention fuel resources.

6.2.4. Kinetics and mechanisms

In the thesis, the kinetics and mechanisms have not been investigated. There are some conflicts between the proposed different mechanisms by far, where the main difference between Langmuir-Hinshelwood and Eley-Rideal mechanisms is whether both methane and oxygen adsorb on the catalyst surface or only the adsorbed oxygen reacts with gaseous methane. And the reaction rate for these two mechanisms is relevant to the partial pressure of methane and oxygen. The Mars-van-Krevelen mechanism, widely accepted in the open literature, believes that oxygen vacancies over the surface of PdO_x crystallites play an important role due to the formation of Pd-O bonds. It is reported that reaction order of oxygen over the Pd/Al_2O_3 catalyst is equal to 0.04, whereas methane reaction order is 0.62. The reaction order of oxygen increased to 0.23 in the $Pd-Co/Al_2O_3$ catalyst and the methane reaction order decreased to 0.59, which might be due to that Co^{2+} activated more active oxygen species over the catalyst surface [48]. This suggested that the reaction followed the Langmuir-Hinshelwood mechanism over these two catalysts. However, as for Pd-Co-DEG (diethylene glycol)/Al_2O_3 catalyst, the reaction followed the Mars-van-Krevelen mechanism because the Pd-O bond formed via reacting with the adsorbed methane, and the partial pressure of oxygen presented a little influence on the reaction rate. Future investigations on the kinetic parameters and mechanisms over various catalysts, especially on the bimetallic catalysts (e.g., Pt-Ni, Pt-Fe, etc.), are still required.

6.2.5. Mass transfer characterization

In the current thesis, the mass transfer characteristics have been briefly discussed on both the capillary and plate-type microreactors. Future investigations on the mass transfer could be focused on: (1) the internal diffusion as a function of the Pt/ γ-Al_2O_3 coating properties (e.g., thickness, pore structure, Pt particle size) subject to different coating preparation methods, and their quantitative influence on the CMC reaction. (2) the gas-solid mass transfer models to be built up for different reaction microchannel configurations, which requires a good understanding in the flow behaviour of the reactant mixture as well. (3) The simulation studies on the flow and temperature profiles over various geometries of micro reactors under different

reaction conditions (e.g., flow rate, $O_2:CH_4$ molar ratio) , and their influence on mass transfer and reaction in order to compare with the experimental work presented in Chapter 5.

6.2.6. Partial methane oxidation

The partial methane oxidation under molar ratios of $O_2:CH_4 < 2$ has been briefly mentioned in the PhD thesis (Chapters 4 and 5), over the same $Pt/\gamma\text{-}Al_2O_3$ catalyst. The proportion of CO_2 in the product is too high in our experiments, which results in the undesirable synthesis gas ratio of H_2/CO. It might be due to the unfavorable reactant ratio and unsuitable catalyst that result in the overoxidation of products. Many interesting works remain to be performed in this respect in order to generate the syngas. Effect of the reactant ratio, pressure, temperature and mechanisms on the product selectivity has been evaluated in many earlier studies [49-51]. The carbon deposition over the catalyst mainly due to thermal decomposition of CH_4 and CO at high temperatures will easily result in the catalyst deactivation. Moreover, special attention is needed on the influence of different CH_4/O_2 ratios on the product selectivity distribution, and an H_2/CO ratio of 2 is ideal for downsteam processes for methanol synthesis.

6.3. Future prospects for long term research

6.3.1. Catalysts

The mixed oxide catalysts have not been involved in this PhD thesis despite that they play an important role in this field. Regarding the hexaaluminate, a great effort has been made on improving the specific surface area and catalyst activity, but many more efforts are still required in future studies so as to improve the catalyst activity. It could be summarized as follows. (1) The highly dispersed noble nanoparticles supported on hexaaluminates with the high specific surface area is expected to develop further in details. The high dispersion of active centres after reduction could be formed via the high-dispersion noble nanoparticles in the structure of hexaaluminates, which significantly improves the catalyst activity. (2) Co-substituted metal alloys could be formed via bi-/triple-noble nanoparticles supported on hexaaluminates, and the structure of hexaaluminate catalyst might be modified, which probably improves the catalyst activity towards the targeted reactions. The fundamental understanding and investigations on the surface structure of hexaaluminates with substituted metals are still lacking, especially on the coherent relationship between the noble-metal substitution, oxygen vacancies, active oxygen species and catalyst activity. Moreover, the interaction between active sites and reactants (or intermediates) is still not clear. (3) The improvement of the specific surface area could be achieved by preventing the particle growth during the crystallization. It has been

reported that the calcination procedure could be operated under inert atmosphere for the crystallization process before removing the template, which may effectively suppress the growth and agglomeration of particles [52]. More studies on the preparation methods are still required, especially on how to increase the specific surface area.

Regarding the perovskite catalyst, a significant progress has been reached for the CMC. Some promising directions for perovskite catalysts may be summarized as follows for the potential industrial applications. (1) The three-dimensional perovskite with hierarchically porous structure exhibited a superior catalytic activity, which could be attributed to the maximized exposure of active sites over the catalyst surface with abundant internal space to accommodate the reactants. Given this unique structure and desirable specific surface area, the well-defined porous structures with layered three-dimensional perovskites could be a very attractive direction for the next generation of high-activity catalysts. (2) Various morphologies of perovskite catalysts with regard to their influence of the catalytic activity are interesting to be investigated, such as nanowire structure, layered nanostructure. However, the structure collapse induced by the reduced activity of nanostructured perovskite catalysts might hinder further applications, which is also a challenging barrier to be overcome. (3) The principal influence of foreign-cation substitution on oxygen mobility and redox property is still unknown. The investigation needs to be performed on the intercontact between oxygen vacancies, lattice oxygen mobility and surface adsorbed oxygen. This is crucial for the catalyst activity because it could offer an in-depth understanding of the reaction mechanism. Moreover, the development of the new substitution systems with inexpensive material is also needed in order to improve the catalyst activity and reduce the cost.

6.3.2. Catalytic methane combustion coupling with endothermic reactions

In this section, the representative (micro)reactors coupling the CMC with different endothermic reactions are discussed, which could be considered as one of the most promising applications in the future [53].

6.3.2.1. Different reactors

The principle of coupling reactions is to maintain the system energetically self-sustaining by employing the heat generated from an exothermic reaction to drive an endothermic reaction. The reactor design, the energy conservation, the boundary conditions, etc., are main factors to cope with. In this section, the representative type of reactors and endothermic reactions are typically addressed.

As for regenerative coupling reactor, the exothermic and endothermic reactions alternatively happen in the same catalytic reactor. Temperature distribution along the reactor becomes more complex due to the continuous switching between the exothermic and endothermic reactions as well as the (significant) heat losses. Meanwhile, such frequent switching in the heating and cooling process easily results in the rapid damage of catalyst activity.

As for the direct coupling reactor, the exothermic and endothermic reaction take place at same time in the same catalytic reactor but without a separating wall between the reactions [54]. The reduction of heat losses between exothermic and endothermic reactions due to the direct heat exchange is one of main advantages of this type reactor [55]. The applied catalysts with bifunctions are one of the major concerns herein because the catalysts have to favor both exothermic and endothermic reactions.

As for the recuperative coupling reactor, both the exothermic and endothermic reactions take place in the same reactor but the conductive walls are applied between two reactions to transfer the released heat [53,54]. The process of heat exchange in the reactor can be performed in the different flow modes (e.g., co-current, counter-current), offering the respective advantages (and disadvantages). The outlet gases in the exothermic and endothermic reactions are able to be separated in this type of reactor, which is beneficial for the energy recovery and gas collection (e.g., H_2, synthesis gas from methane steam reforming). Therefore, more studies could be carried out on the following aspects:

(1) As for the direct coupling reactor, due to the reactant mixing, the products from the outlet stream collect from both reactions. Commonly the membrane reactor could be introduced at the end of reactor in order to collect and separate the hydrogen as the desire product (methane steam reforming as the endothermic reaction). As for the recuperative coupling in the microreactor, studies are mainly focused on the numerical simulations in order to investigate an optimized flow direction mode for the favourable energy supply. In order to obtained the higher yield, the multiple stacked microchannel reactors by coupling the methane combustion with the endothermic reaction are recommended, but rarely tested experimentally so far.

(2) The experiment results reported by Yin et al. [56] exhibited that it might be unable to accomplish the coupling of CMC with methane reforming (with CO_2) without additional heat supply. Thus, the extra heat source has to be introduced in order to maintain the whole energy balance of the system. Attention should also be paid to the selection of reactor material. The stainless steel with the relatively good heat conductivity enables to limit the formation of

hotspots, but on the other hand the heat losses could be greatly increased [57,58]. Thus, the reduction of surface to volume ratio, the utilization of the high insulation and high reflectance materials [59,60], the vacuum operation [61,62], etc., could be the possible solutions to reduce the thermal losses.

(3) The flow direction is another important parameter to be considered in the recuperative reactor, which could significantly influence the conversion of reactants. With respect to the co-current mode, the higher average temperature and reaction rate could be reached than the counter-current mode [63-65], and the hot spots and cold spots might be more easily to be formed under counter-current conditions. The alternative solutions could be the optimization of the catalyst location, the thickness (e.g., single/multi-layer systems) in the autothermal (micro)reactor. Meanwhile, the less amount of catalysts may be placed in the potential hotspots, and vice versa, in order to balance the temperature profile along the reactors.

(4) The actual temperature inside the catalysts/channel might be significantly different from the measured temperature by thermocouples on the catalysts/channel surface (in microreactors). Thus, the simulation results being predicted based on the experimental temperature could be different from the actual conversion values. One of the possible approaches is to employ the infrared camera mapping the actual temperature during the reaction. Thus, at least one side of reactor walls must be composed of a transparent material (e.g., quartz) to allow the optical visibility. While carrying out the experiment in the optically accessible reactor, the temperature profile could be clearly observed by the infrared temperature measurement on the catalyst surface [66]. In this way, a great number of mapping points at different positions of reactors could be collected, offering a more accurate reference to discriminate between the different mass/heat transfer models and preventing the errors in the fitted kinetic parameters.

(5) The experiment investigations would be very attractive for plate-type microreactors with alternate stacks (i.e., one above another) by combining the catalytic methane combustion with endothermic reactions. The modelling studies have been performed by e.g., Mundhwa et al. [65,67]. However, more experiment work needs to be carried out to verify the modelling results published in the literature. Typically, the actual heat and mass transfer models could be built up based on the experiment data under different conditions. This could provide a useful guideline for the scale-up of such microreactor systems aiming at industrial applications of the CMC in the future.

6.3.2.2. Representative endothermic reactions

Some representative endothermic reactions are commonly used for coupling with the CMC, such as the methane steam reforming, methane reforming with CO_2, dehydrogenation of propane to propylene, etc. One of the main applications of methane autothermal reforming is to produce the synthesis gas with high H_2/CO ratio by utilizing the energy from the CMC. A selective membrane is commonly used to remove some of the undesired product gases, so as to obtain highly-purity hydrogen from the endothermic reaction. The applied catalysts in the recuperative coupling reactor could be designed independently for exothermic and endothermic reactions. Commonly, Pt-Ni pair is one of the most frequent combinations. However, on the endothermic side, the coke formation of the catalyst is still a main challenge for methane steam/CO_2 reforming reaction [68,69]. It has been reported that the addition of Rh to Ni-/Mg-based catalysts is able to prevent the coke formation [68,69], and the bifunctional catalysts is still need to be well developed in the future.

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