Minimizing carbon deposition in plasma-induced methane coupling with structured hydrogenation catalysts

Nuria García-Moncada a,1, Toine Cents b, Gerard van Rooij c, Leon Lefferts a,*

a Catalytic Processes and Materials (CPM), TNW Faculty, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
b Sasol Holding Netherlands B.V., 7544 GG Enschede, The Netherlands
c Catalytic Processes and Materials (CPM), TNW Faculty, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Article info

Article history:
Received 1 May 2020
Revised 31 August 2020
Accepted 6 September 2020
Available online 11 September 2020

Keywords:
Dielectric barrier discharge (DBD) plasma-catalysis
Structured reactor
Methane coupling
H2 co-feed
Temperature optimization
Carbon deposits

Abstract

The effect of temperature and hydrogen addition on undesired carbonaceous deposit formation during methane coupling was studied in DBD-plasma catalytic-wall reactors with Pd/Al2O3, using electrical power to drive the reaction. Experiments with thin catalyst layers allowed comparison of the performance of empty reactors and catalytic wall reactors without significantly influencing the plasma properties. The product distribution varies strongly in the temperature window between 25 and 200 °C. Minimal formation of deposits is found at an optimal temperature around 75 °C in the catalytic-wall reactors. The selectivity to deposits was c.a. 10% with only 9 mg of catalyst loading instead of 45% in the blank reactor, while decreasing methane conversion only mildly. Co-feeding H2 to an empty reactor causes a similar decrease in selectivity to deposits, but in this case methane conversion also decreased significantly. Suppression of deposits formation in the catalytic-wall reactor at 75 °C is due to catalytic hydrogenation of mainly acetylene to ethylene. In the empty reactor, H2 co-feed decreases conversion but does not change the product distribution. The catalytic-wall reactors can be regenerated with H2-plasma at room temperature, which produces more added-value hydrocarbons.

© 2020 The Authors. Published by ELSEVIER B.V. and Science Press on behalf of Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Availability of large natural gas reserves rich in CH4 and, more recently, the development of shale gas in USA, has revived interest in developing direct routes for methane conversion to higher value chemicals [1,2]. Oxidative and non-oxidative coupling of methane has been extensively studied [3,4]. However, the former struggles with extensive deep oxidation to CO and CO2, while the later suffers from carbon formation, low methane conversion and high operation temperatures (>600 °C). Consequently, non-oxidative coupling of methane via non-equilibrium plasma is attracting attention in the last decades [5–8], offering an avenue to electrify the chemical industry by using electrical power to drive an endothermic and endogenic reaction. Methane coupling in a dielectric barrier discharge (DBD) reactor is possible at mild temperatures close to ambient [8,9] without the need of a catalyst.

Electrons with high energy (~1030–104 K) are capable of activating methane molecules by electrons impact, creating radicals (CH4 + e− → CH3 + H + e−) [8].

High methane conversion is achieved by plasma depending on the discharge power, the feed composition (pure or diluted methane with noble gas, or additives like H2 or H2O) and the reactor design [10–14]. However, as plasma activates methane via formation of radicals, the selectivity to desired products cannot be controlled. Formation of several linear or branched hydrocarbons have been reported, usually between C2 and C6, depending also on the power and the feed composition [15–17]. In general, most papers report only the selectivity to desired hydrocarbons, without explicitly considering the carbon balance and carbon formation. However, formation of carbonaceous deposits is significant and increases on increasing conversion [7,18–21]. Jo et al. [12,14,22] reported poor carbon balances between 70% and 75%, excluding deposits, at 20% CH4 conversion in different noble gases. Wang et al. [11] studied methane conversion and the selectivity to carbon deposits at different reactor conditions (residence time, power, discharge gap) at typically 20% conversion. The formation of carbon was measured by weighing the reactor before and after the exper-
iment but unfortunately, the resulting carbon balance was still below 70%. Indarto et al. [17] reported formation of carbonaceous deposits on the wall of a DBD plasma reactor causing deactivation, even under favorable conditions to minimize carbon formation, i.e., at methane conversion as low as 13.8%. Our group reported recently on application of a catalytic-wall reactors to combine catalyst and DBD plasma [23]. The selectivity to carbonaceous deposits was below 5% at 34% methane conversion with a carbon balance of 93%, by using 15 mg of Pd/Al_{2}O_{3} catalyst in a 2.8 W DBD reactor at room temperature. Operation without catalyst under the same condition resulted in more than 17% selectivity to deposits [23].

Combining plasma and catalysis is rather complex to understand [24–27]. However, the presence of the catalyst can contribute to methane activation and/or selectivity to desired hydrocarbons, decreasing the formation of deposits [8,23,28]. According to our previous work [23], catalytic-wall reactors only mildly influence plasma properties and methane conversion level, strongly acting on the product distribution when using a hydrogenation catalyst, e.g., based on Pd. Although Pd-based catalyst cannot activate methane at mild temperatures, Pd was used in combination with DBD in post-plasma configuration [21], resulting in hydrogenation of acetylene to ethylene as would be expected based on the fact that Pd-based catalysts are industrially applied for hydrogenation of traces of acetylene in ethylene at mild temperatures [29]. Similarly, Jo et al. [22] studied the performance of a planar DBD reactor in non-oxidative coupling of methane with Pt/Al_{2}O_{3} compared to the bare Al_{2}O_{3} support. The presence of Pt decreased the conversion slightly while the product distribution shifts to more saturated hydrocarbons, which was attributed to lowering the electric field in the presence of Pt. Surprisingly, the fact that Pt is one of the most active catalysts for hydrogenation reactions was not considered. Górska and co-workers [30] studied the performance of Cu/ZnO/Al_{2}O_{3} pellets in a DBD reactor at 240 °C. However, the comparison between the catalytic-plasma configuration, the blank reactor and a packed bed DBD reactor with catalytically inert glass, all showed similar conversion and selectivities at this temperature and conditions. Moreover, the discharge power, formation of carbon deposits and the carbon balance were not reported; so it remains unclear whether any catalytic effect occurred.

The goal of this work is to study the effect of temperature and H_{2} co-feeding in DBD plasma-catalysis reaction when Pd/Al_{2}O_{3} catalyst is used inside the plasma zone for non-oxidative coupling of methane, mainly aiming at decreasing the formation of carbonaceous deposits and improving the stability of the catalyst. In order to minimize the influence of the catalyst on the plasma and to observe the catalytic effect, catalytic-wall reactors are used, similar to our previous work that was limited to operation at room temperature.

2. Experimental

Coupling of methane reaction was performed in a home-made DBD plasma reactor at atmospheric pressure. A quartz tube of 4 mm inner diameter, 6 mm external diameter and 30 cm in length was used as a reactor as well as dielectric material. Two coaxial stainless steel electrodes (a rod 1.6 mm in diameter in the center of the reactor and an external cylinder 3.3 cm in length enclosing the quartz tube) were connected to an AC voltage supplier (PVM/DDR Plasma Driver GME P89 CLASS 2.5) to provide the discharge. The data were collected with an oscilloscope (Pico Scope 2000 series) connected to a high voltage probe (TESTEC TT-HVP15 HF), a 3.9 nF capacitor and a probe (TESTEC TT-HV 250) linked to the grounded electrode as is depicted in Fig. 1. The discharge power in the reactor gap was calculated based on Q-V Lissajous plots [31,32]. The plasma-assisted reaction was tested at different temperatures using a cylindrical oven around the reactor, measured with a thermocouple placed next to the grounded electrode.

A mixture of 6% CH_{4} in Ar was fed with a flow rate of 20 mL min^{-1} in the DBD plasma reactor (volume of the plasma zone 0.35 cm^{3}), fixing the residence time at ~1 s. The outgoing gas phase was analyzed with an online Varian 450 GC equipped with TCD and FID detectors and Hayesip T&Q, Molsieve 13x and PoraBOND Q columns with programmed temperature control. For identification and quantification purpose, the GC was calibrated with several gas mixtures with known composition. Unconverted CH_{4} as well as the product mixture of H_{2}, C_{2}, C_{3} and C_{4} hydrocarbons were quantified. The methane conversion, carbon-based hydrocarbon selectivities and hydrogen selectivity were calculated as follows:

\[ \text{Conv}_{\text{CH}_{4}}(\%) = \frac{n_{\text{IN}}}{n_{\text{IN}}} - \frac{n_{\text{OUT}}}{n_{\text{IN}}} \times 100 \]  

\[ S_{H_{2}}(\%) = \frac{x \cdot n_{H_{2}}}{n_{\text{IN}}} \times 100 \]  

\[ S_{C_{n}H_{m}}(\%) = \frac{1}{x} \cdot \frac{n_{C_{n}H_{m}}}{n_{\text{IN}}} \times 100 \]

where \( n_{i} \) is the molar concentration of each compound (hydrocarbons or hydrogen) and \( x \) is the number of carbon atoms in \( C_{n}H_{m} \). The change in the molar flowrate is so small that it can be neglected in these calculations. Formation of solid deposits was also observed during the reaction on both the central electrode surface as well as on the internal wall of the quartz reactor. The selectivity to these carbonaceous deposits at a specific time-on-stream is estimated based on the carbon balance of conversion of methane and formation of products, with a maximal accumulated error margin of c.a. 20%, assuming that missing carbon is completely converted to deposits (principle of mass conservation):

\[ S_{C_{n}H_{m}}(\%) = 100 - \sum S_{C_{n}H_{m}} \]  

2.1. Temperature effect at different power discharges

The effect of the temperature was measured in a blank reactor, without catalyst, as well as in catalytic-wall reactors with thin layers of commercial Pd/γ-Al_{2}O_{3} catalyst (1 wt% Pd, Alfa Aesar) on the internal wall of the quartz reactors. As described previously [23], washcoating of the internal quartz wall was achieved using Pd/γ-
Al_2O_3 catalyst particles smaller than 32 μm, obtained via sieving. The resulting structured reactors contain a 19 to 24 μm thick homogeneous catalyst layer of 3.3 cm in length, exactly coinciding with the discharge area. Thus, the residence time in the discharge volume is not significantly influenced by the presence of the thin catalyst layer, remaining 1 second in all cases.

Coupling of methane was carried out between room temperature and 200 °C and discharge powers between the breakdown voltage (–1.8 kV) and 2.5 kV at fixed frequency of 23 kHz. The plasma was switched off when changing temperature, in order to minimize deactivation by carbon deposition. The plasma was switched on after stabilization of the temperature, followed by GC sampling 2 minutes later.

The deactivated reactor was regenerated in 1.5 W of power discharge in 20 mL min⁻¹ of 10% of H2 (balanced with Ar) at ambient temperature and pressure for 2 h, in order to remove the carbon deposits. Thereafter, performance for methane coupling was measured again.

2.2. H2 effect at different temperatures

The effect of H2 co-feeding (0.3% and 6% H2) on performance was measured at furthermore identical conditions (fixed 6% CH4 balanced with Ar, total flow rate of 20 mL min⁻¹, residence time of 1 s). Temperature was varied between room temperature and 200 °C, keeping the plasma power constant at 1.5 W. The catalytic wall reactors in these experiments contained c.a. 5 mg of commercial Pd/Cy-Al2O3 forming a 12 μm thick layer.

2.3. Stability tests

The stability of the performance in terms of plasma power, activity and selectivity was measured during 190 minutes in the catalytic-wall reactor operated at 75 °C, using a fresh catalytic-wall reactor with similar catalyst loading of c.a. 9 mg. For comparison, the blank reactors with and without H2 co-feeding (6%) were also tested in the same conditions. Both experiments were performed with a total flow rate of 20 mL min⁻¹ and 6% CH4 concentration at atmospheric pressure, residence time of 1 second and 1.5 W of discharge power and 23 kHz AC frequency.

In addition to the analysis procedure for calculating the selectivity towards deposits at a specific time-on-stream outlined above, the averaged selectivity to deposits was calculated after each experiment based on the amount of deposits. This was determined by weighing the electrode and the reactor before and after the experiment, allowing calculation of the amount of deposits with an accuracy of ± 0.1 mg. The C- and H-content in the yellowish deposits formed on wall of the quartz tube is calculated based with an accuracy of ±0.1 mg. The C- and H-content in the yellowish deposits formed on wall of the quartz tube is calculated based on CHN elemental analysis (Organic Elemental Analyzer, Flash 2000, Thermo Fisher Scientific Inc.). The averaged selectivity to deposits is then calculated according:

\[
S_{\text{Dep, Average}}(\%) = \frac{\text{n}_{\text{Ce}} + \text{n}_{\text{Cq}}}{\text{Conv}_{\text{CH4}} \cdot \text{t} \cdot \text{CH}_4 \cdot \text{A}} \times 100
\]

where \(n_{\text{Ce}}\) and \(n_{\text{Cq}}\) are the number of moles carbon deposited on the electrode surface and the number of moles C in the polymeric deposit on the quartz wall, respectively. \(\text{Conv}_{\text{CH4}}\) is the average conversion during 190 min of reaction, \(f_{\text{in}}\) is the inlet molar flow rate of methane and \(t\) is the reaction time (190 min). Hydrogen and carbon balances in these experiments were calculated based on the amount of deposits detected after the full experiment, combined with the integrated amounts of products and unconverted methane as determined by GC during the experiment:

\[
\text{C}_{\text{Bal}} = \sum \left( x \times \frac{F_{\text{out,CH4}}^{\text{out}}}{F_{\text{CH4}}} + \frac{\text{n}_{\text{C1}}^t + \text{n}_{\text{C2}}^t}{F_{\text{CH4}}} \right)
\]

\[
\text{H}_{\text{Bal}} = \sum \left( y \times \frac{F_{\text{out,CH4}}^{\text{out}}}{F_{\text{H2}}} + \frac{2 \times F_{\text{out,H2}}^{\text{out}}}{F_{\text{H2}}} + \frac{1.7 \times \text{n}_{\text{Cq}}}{F_{\text{CH4}}} \right)
\]

The factor 1.7 in Eq. (7) is based on elemental composition of the yellowish deposits on the internal surface of the quartz tube.

3. Results

3.1. Effect of temperature at different powers

The effect of the discharge power on methane conversion is plotted in Fig. 2, at different temperatures for both the blank reactor (Fig. 2a) and a catalytic-wall reactor containing 7.8 mg catalyst (Fig. 2b). Fig. 3 shows the methane conversion and the product distribution grouped in saturated hydrocarbons (C,H₆, C,H₈, n-C₄H₁₀, iso-C₄H₁₀), unsaturated hydrocarbons (C,H₄, C,H₂, C,H₈, 1-C₄H₈, 1,3-C₄H₆ and deposits for 0.9 W and 1.3 W discharge powers, for both blank reactor and the catalytic-wall reactor.

Methane conversion increases on increasing discharge power in all cases, as shown in Fig. 2. On the other hand, temperature increase mildly enhances the conversion in the blank reactor (Figs. 2a, 3a and b), whereas the catalytic-wall reactor shows no clear trend (Figs. 2b, 3c and d). In fact, the conversion seems to increase when increasing temperature from ambient to 50 °C, but is clearly decreasing when heating further to 100 °C. At higher temperatures, the trend is similar to the blank reactor, i.e. increasing temperature further is boosting methane conversion.

In general, higher power and consequently higher methane conversion, always favors formation of carbonaceous deposits in both reactors, decreasing the selectivity to desired hydrocarbons. However, the product distribution in the gas phase, i.e. the ratio between saturated and unsaturated hydrocarbons, is not significantly influenced (not shown).

The product distribution is significantly influenced by temperature in the catalytic reactor (Fig. 3c and d), while a much smaller effect is observed in the blank reactor (Fig. 3a and b). The selectivity to saturated hydrocarbons, mainly ethane, is maximal at 100 °C in the catalytic reactor, mainly caused by a decrease in selectivity to deposits, independently of the discharge power used.

Fig. 4 shows the result of a similar experiment with a catalytic-wall reactor containing 9.6 mg catalyst at higher discharge power (1.5 W), measuring at more temperatures and also varying the order of measurements, i.e. starting at the highest temperature. The same trends in conversion and selectivity are observed and the minimal selectivity to deposits is obtained at 75 °C.

The similarity of the results in Fig. 4, compared to Figs. 2 and 3, demonstrates that formation of deposits can be diminished by mildly heating the catalytic reactor, independent of power and the exact amount of catalysts. Importantly to note, effects of changing performance over the course of the measurements was excluded.

Fig. 5 shows that operation of the catalytic-wall reactor during the experiments reported in Figs. 3 and 4, followed by several experiments to ensure reproducibility (not shown), finally results in deactivation after days of experiments. The typical profile in the product distribution with temperature almost disappeared, indicating deactivation of the hydrogenation catalyst. However, the profile was significantly recovered by the treatment in H₂ plasma as is described in section 2.1. Fig. 5(b) shows a more detailed comparison of the same data for the fresh, used and regenerated catalytic-wall reactor at 75 °C and 100 °C, showing similar
conversion in all three experiments. In contrast, the product distribution varies significantly at similar conversion levels. In addition, small amount of methane and C₂ hydrocarbons were observed during exposure of the deactivated reactor to the hydrogen plasma (not shown).

### 3.2. Effect of hydrogen

As regeneration of deactivated catalyst was achieved with H₂ plasma, the influence of H₂ co-feeding was assessed, as shown in Fig. 6. The temperature was varied between room temperature and 200 °C at fixed discharge power of 1.5 W, using catalytic-wall reactors containing ~5 mg Pd/γ-Al₂O₃ implying a catalyst layer of ~12 μm. The H₂ concentration was varied between 0 and 6%, while keeping the CH₄ concentration at 6%, balanced with Ar.

Addition of H₂ decreases the methane conversion, i.e. 25% > 18% > 12% conversion for 0%, 3% and 6% H₂, respectively (Fig. 6a, c, e). The selectivity to deposits at room temperature decreases significantly on addition of H₂ (Fig. 6b, d, f), causing disappearance of the typical profile of selectivity with temperature, with a clear minimum at 75 °C. A minor effect on product distribution is observed between 25 and 75 °C, whereas formation of deposits remains suppressed also at higher temperatures when H₂ is added.
3.3. Stability at 75 °C

The stability at 75 °C was tested by running experiments during 190 minutes, comparing the empty reactor with the two cases achieving suppression of formation of deposits, i.e. the catalytic wall reactor and the empty reactor operated with 6% H₂ in the feed. Plasma power, methane conversion and product distribution were measured as presented in supporting information, Figs. S1–S3. Fig. 7 summarizes the observations by comparing the conversion and product distribution after 10 minutes and 190 minutes TOS for all three cases. In addition, the amount of carbon deposits on the central electrode as well as the amount of the polymeric deposits on the quartz wall, formed during the 190 minutes experiment, were measured by weighing (Table 1). The averaged carbon selectivity is calculated according to Eq. (5), considering the black deposits on the central electrode as pure carbon whereas the C content of the deposit formed on the quartz internal surface was calculated based on the CHN elemental analysis, resulting in a C/H molar ratio of 1/1.7.

The discharge power is remarkable stable in Fig. 7. Accordingly, the methane conversion, which is due to the methane activation by plasma, is also quite stable considering a typical error margin of 5% in these measurements as reported earlier [23]. Furthermore, the methane conversion is not significantly changed by the presence of the catalyst (Fig. 7a and c). In contrast, the catalyst decreases the selectivity to deposits with a factor of 2, while increasing the selectivity to alkanes. On the other hand, addition of H₂ to the blank reactor (Fig. 7b) causes a similar decrease in the selectivity to deposits (factor 1.15), but in this case also the methane conversion decreases at least to the same extent. In other words, the suppression of formation of deposits obtained by H₂ addition in the empty reactor in Fig. 7(b), is similar to the effect obtained with addition of catalyst in absence of H₂ (Fig. 7c). However, the addition of catalyst is more attractive than H₂ addition because the conversion level is retained at 25%, while addition of H₂ decreases the conversion to 10%. For comparison purposes, Fig. 8 shows the effect of hydrogen addition to the empty reactor, keeping the methane conversion constant by adjusting the plasma power.

Table 1 reports time-averaged selectivities to deposits based on weighing. The data confirm that addition of catalyst suppresses the formation of deposits by catalytic hydrogenation. H₂ also reduces the absolute amount of deposits formed in the blank reactor, but at the expense of lowering methane conversion resulting in a relatively high selectivity to deposits. Note that the mass balance closes remarkably well, especially for the case of the blank reactor with addition of hydrogen.

Also, the product distribution varies only mildly with time-on-stream during 190 minutes TOS (Figs. S1–S3). The catalytic-wall reactor produces the most saturated hydrocarbons and ethylene, minimizing acetylene yield to c.a. 1%.

4. Discussion

Fig. 2 shows that the methane conversion increases with plasma power both in absence and presence of catalyst, as expected because energetic electrons in the plasma activate methane molecules, followed by radical reactions towards products [8,12,15,28]. The detailed mechanism [8,16,17,33–36] of this reaction is outside the scope of this study. However, Fig. 3 shows that increasing power also increases the formation of deposits, which also agrees well with other studies [7,11,37,38].

On the contrary, the presence of catalyst strongly influences the effect of temperature on performance. The empty reactor (Figs. 2a, 3a and b) shows a mild increase in conversion with temperature, as well as small changes in the product distribution. In contrast, tem-
perature has a prominent effect on the performance of the catalytic-wall reactor. Selectivity to deposits is minimal, selectivity to alkanes is maximal, whereas conversion shows a less prominent minimum between 75 and 100 °C (Figs. 2–4), independently of the amount of catalyst and plasma power.

In our previous work on Pd/γ-Al₂O₃ catalytic-wall reactors for coupling of methane in DBD-plasma [23], we attributed the effect of catalyst on methane conversion to Pd catalyzed hydrogenation of methyl radicals produced in the plasma at the external surface of the catalytic wall. The minor effect of temperature on methane conversion is probably the result of increasing conversion in the plasma, as discussed above, and increasing hydrogenation of CHₓ radicals on the outer surface of the catalyst layer [23]. The suppressing effect of the catalyst on carbon deposition, accompanied by suppressing of acetylene formation (see Fig. S4) and enhancement of alkane formation, was attributed to hydrogenation of acetylenes on Pd [23], thereby preventing oligomerization of acetylenes [8,39] as a consecutive reaction. The results in Figs. 2–4 reveal that this effect is maximal between 75 and 100 °C, which agrees well with the fact that Pd based catalysts perform optimal for acetylene hydrogenation at temperatures around 70 °C [29]. Thus, the conversion of methane is dominated by plasma, which has a fairly constant discharge power at all temperatures, resulting in similar conversions. When methane is activated in the plasma, catalyzed hydrogenation reactions are particularly enhanced at temperatures between 70 and 100 °C, due to both thermal-catalytic hydrogenation of acetylene as well as plasma-catalytic hydrogenation of radicals. Hence, acetylene is mainly hydrogenated to ethylene, also increasing the production of ethane via consecutive hydrogenation and decreasing the formation of depos-

Fig. 6. The effect of temperature on discharge power, methane conversion and product distribution in catalytic-wall DBD reactors at 1.5 W at different H₂ concentrations.
its via acetylene oligomerization. We can however not rule that catalytic hydrogenation of acetylene radicals and/or reaction of deposits with plasma activated species, e.g. H-radicals, also contribute to decrease the formation of deposits.

| Experiment          | Deposits on quartz (mg) | Deposits on electrode (mg) | C_{rel}  | H_{rel}  | Selectivity (%) |
|---------------------|-------------------------|---------------------------|----------|----------|-----------------|
| Blank-0%H₂          | 5.1                     | 0.7                       | 0.95     | 0.99     | 19.9            |
| Blank-6%H₂          | 1.6                     | 0.4                       | 0.99     | 1.00     | 15.5            |
| Cat.Wall-0%H₂       | 1.9                     | 0.3                       | 0.95     | 0.99     | 7.0             |

* Standard deviation 0.01;

Selectivity calculated based on weights of deposits and CHN analysis, using Eq. (5).

Fig. 7. Discharge power (right axis), methane conversion (left axis) and product distribution (left axis) at 10 and 190 min of stability tests in a blank reactor (a), a blank reactor co-feeding 6% H₂ and in the catalytic-wall reactor (c) at 1.5 W, 75 °C, 6% CH₄. Selectivity to deposits estimated using Eq. (4).

Fig. 8. Comparison of the product distribution (a) in groups and (b) in detail of blank reactors without and with 6% H₂ co-feed at the same methane conversion level and reaction conditions (6% CH₄ balanced with Ar, 20 mL min⁻¹ total flow, 1 s of residence time, atmospheric pressure, after 22 min of reaction). Conversion level obtained particularly at 0.7 and 1.8 W in absence of hydrogen (0%) and with 6% H₂, respectively. Selectivity to deposits calculated by Eq. (4).
Clearly, the activity of the Pd catalyst for hydrogenation of unsaturated hydrocarbons is affected when exposed to methane plasma for a long time (Fig. 5), caused by carbon deposition. The catalyst can be partly regenerated in H2 plasma, probably via H- radicals reacting with C deposits, similar to H2 activation by plasma reported in different reactions or for reducing surfaces [40–44]. This is confirmed by the fact that hydrocarbons, mainly methane, are formed during the H2-plasma treatment, proving hydrogenation of carbonaceous deposits. Hence, regeneration enables not only recovery of the catalytic activity but also generates compounds with value, in contrast to oxidative regeneration producing CO2 [45].

Fig. 6 shows that addition of H2 to the catalytic wall reactor further suppresses formation of deposits and unsaturated hydrocarbons, favoring formation of saturated hydrocarbons, at the expense of further decreasing methane conversion. The extra hydrogen radicals, generated upon the H2 supply, enhance recombination between the H radicals and the C-containing radicals, effectively suppressing the cleavage of C–H bond in methane as well as C–C bond coupling, in addition to decreasing the formation of acetylene and deposits. This is all in line with the discussion so far, the only difference being that hydrogen is now available everywhere at high concentration, instead of being formed in the methane coupling reaction. The hydrogenation capacity is now sufficient to induce the same effects even at room temperature. The further decrease in methane conversion indicates that hydrogenation of CHx radicals is also enhanced, or that part of the plasma power is diverted to H2 activation, decreasing the specific energy input (SEI) to methane.

Fig. 7 presents the performance of the catalytic reactor at optimal conditions (75 °C and 1.5 W) based on the data presented in Figs. S1–S3, revealing not only stability of the operation during 3 hours, but also allowing measurement of the amount of deposits formed based on weight. The empty reactor was also tested under the same conditions, both with and without H2 co-feeding. In general, methane conversion decreases mildly with time on stream (TOS) and this effect is significantly weaker compared to previous results obtained with higher power (2.8 W) and consequently higher methane conversion [23]. Also, the decrease in power with TOS, if any, is much weaker. This is attributed to the formation and accumulation of deposits [21,23] based on the observation that losses in power and conversion with TOS can be mitigated via decreasing the formation of deposits, e.g. by adding more catalyst as demonstrated previously [23]. Conductive deposits and filaments suppress formation of streamers in the gas volume, decreasing the intensity of the plasma. Fig. 7 also shows that changes in the product distribution with TOS are also small, the only exemption being the significant increase in the selectivity to unsaturated hydrocarbons (mainly ethylene) and deposits at the expense of formation of saturated hydrocarbons in the catalytic-wall reactor. This is caused by blocking of the active sites for hydrogenation by carbon deposits.

The data in Table 1 confirm that addition of catalyst suppresses the formation of deposits via catalytic hydrogenation, based on the weight of deposits formed. Co-feeding H2 also reduces the absolute amount of deposits formed in the blank reactor, but partially at the expense of also lowering methane conversion. This decrease can only be partly attributed to the decrease in methane conversion as illustrated in Fig. 8, showing data at the same level of methane conversion with and without H2 addition, by adjusting the plasma power. Apparently, the increase in H2 concentration in the plasma favors not only quenching of CHx radicals in the plasma to form methane, but even stronger suppresses the reaction pathway to deposits, in the plasma and/or on the surface of the electrode and the quartz tube. It is striking that the C-mass balance closes excellently for the experiment in presence of H2. This suggests that no higher hydrocarbons are formed that cannot be detected with GC. The closure of the C-mass balance is slightly less in absence of H2 (typically 95%). It may be speculated that some higher hydrocarbons manage to escape from the reactor without being detected by GC, but is should also be noted that a 5% deviation in the C balance is also easily caused by inaccuracy in the GC analysis. Obviously, that would also cause overestimation of the amount of carbon deposits based on mass balance as presented in Fig. 7(a and c). In any case, the averaged selectivity in Table 1, based on Eq. (5), confirms that operation with catalyst suppresses formation of deposits much stronger than adding H2 to the blank reactor.

Hence, from a practical point of view, the catalytic-wall reactor is preferred because methane conversion is not significantly affected while decreasing the formation of carbon deposits (Table 1). On the other hand, the formation of olefins also decreases, decreasing the value of the product mixture. Further optimization is clearly required for any practical applications. Figs. S2 and S3 show that especially the selectivity to acetylene is strongly suppressed by the presence of the catalyst, in contrast to the empty reactor operated with H2 addition. This confirms that acetylene is the dominant precursor for formation of carbon deposits [21,39]. This is also in good agreement with work targeting hydrogenation of acetylene to ethylene on Pd-based catalyst in a post plasma system [21,46] or in the hybrid plasma-catalytic system by gliding discharge [47]. Our results show that similar effects can be obtained via catalytic reaction inside the plasma, in a single reactor without addition of any hydrogen, using produced H2 instead.

5. Conclusions

The effect of discharge power, temperature and hydrogen co-feeding on methane conversion, formation of carbonaceous deposits and stability have been studied in a DBD plasma catalytic-wall reactor containing Pd/Al2O3 as well as a blank DBD reactor. Methane conversion is mainly depending on plasma power and much less influenced by temperature in both type of reactors. In contrast, the temperature strongly influenced the product distribution, exclusively in the catalytic-wall reactor. Unsaturated hydrocarbons are hydrogenated on the Pd surface and the kinetics of these reactions is influenced by temperature. Formation of deposit is minimized when operating around 75 °C, while maximizing formation of saturated hydrocarbons. In this way, selectivity to deposits could be reduced to below 10% with less than 9 mg of catalyst loading, while keeping the methane conversion constant at ~25%. Selectivity to carbon deposits can also be suppressed without catalyst by co-feeding H2, but in that case also the methane conversion decreased.

Both systems (catalytic wall reactor and hydrogen addition) exhibited reasonable stability during 3 hours, thanks to the suppression of deposits formation in both cases. In addition, the deactivated catalytic-wall reactor can be regenerated in H2-plasma at room temperature, achieving both recovery of catalytic activity as well as formation of additional valuable hydrocarbons.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Innovation Fund for Chemistry of NWO, grant number 731.014.303, as well as by SASOL. The
authors want to thank Dr. Guido Giammaria for the discussions and Bert Geerdink for the technical assistance.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2020.09.006.

References

[1] J.H. Lunsford, Catal. Today 63 (2000) 165–174.
[2] P. Tang, Q. Zhu, Z. Wu, D. Ma, Energy Environ. Sci. 7 (2014) 2580–2591.
[3] R. Wang, S. Albarracin-Suazo, Y. Pagán-Torres, E. Nikolka, Catal. Today 285 (2017) 147–158.
[4] C. Mesters, Annu. Rev. Chem. Biomol. Eng. 7 (2016) 223–238.
[5] S. Kado, Y. Sekine, T. Nozaki, K. Okazaki, Catal. Today 89 (2004) 47–55.
[6] A. Majumdar, J.F. Behnke, R. Hippler, K. Myataki, R. Schneider, J. Phys. Chem. A 109 (2005) 9371–9377.
[7] F. Saleem, J. Kennedy, U.H. Dahiru, K. Zhang, A. Harvey, Chem. Eng. Process. – Process Intensif. 142 (2019) 107557.
[8] M. Scapinello, E. Delikonstantis, G.D. Stefanidis, Chem. Eng. Process. Process Intensif. 117 (2017) 120–140.
[9] P.J. Bruggeman, F. Iza, R. Brandenburg, Plasma Sources Sci. Technol. 26 (2017) 123002.
[10] S.K. Kundu, E.M. Kennedy, V.V. Gaikwad, T.S. Molloy, B.Z. Drlugogorski, Chem. Eng. J. 180 (2012) 178–189.
[11] B. Wang, W. Yan, W. Ge, X. Duan, J. Energy Chem. 22 (2013) 876–882.
[12] S. Jo, D.H. Lee, K.T. Kim, W.S. Kang, Y.-H. Song, Phys. Plasmas. 20 (2013) 083505.
[13] S. Jo, D.H. Lee, K.T. Kim, W.S. Kang, Y.-H. Song, Phys. Plasmas. 21 (2014) 103504.
[14] S. Jo, D. Hoon Lee, Y.H. Song, Chem. Eng. Sci. 130 (2015) 101–108.
[15] S. Zhang, Y. Gao, H. Sun, H. Bai, R. Wang, T. Shao, J. Phys. D. Appl. Phys. 51 (2018) 274005.
[16] D.H. Lee, K.-T. Kim, Y.-H. Song, W.S. Kang, S. Jo, Plasma Chem. Plasma Process. 33 (2013) 249–269.
[17] A. Indarto, N. Coowanitwong, J.W. Choi, H. Lee, H.K. Song, Fuel Process. Technol. 89 (2008) 214–219.
[18] C. Xu, X. Tu, J. Energy Chem. 22 (2013) 420–425.
[19] J. Liu, Z. Li, J. Nat. Gas Chem. 19 (2010) 375–379.
[20] X.Y. Liu, D.H. Mei, Z. Shen, X. Tu, J. Phys. Chem. C 118 (2014).
[21] E. Delikonstantis, M. Scapinello, G.D. Stefanidis, Fuel Process. Technol. 176 (2018) 33–42.
[22] S. Jo, T. Kim, D.H. Lee, W.S. Kang, Y.H. Song, Plasma Chem. Plasma Process. 34 (2014) 175–186.
[23] N. García-Moncada, G. van Rooij, T. Cents, L. Lefferts, Catal. Today. (2019) In press.
[24] E.C. Neyts, A. Bogaerts, J. Phys. D. Appl. Phys. 47 (2014) 224010–224027.
[25] E.C. Neyts, K. Ostríkov, M.K. Sunkara, A. Bogaerts, Chem. Rev. 115 (2015) 13408–13446.
[26] J.C. Whitehead, J. Phys. D. Appl. Phys. 49 (2016) 243001.
[27] J.C. Whitehead, Front. Chem. Sci. Eng. (2019) 1–10.
[28] T. Nozaki, K. Okazaki, Catal. Today 211 (2013) 29–38.
[29] A. Borodziński, A. Cybulski, Appl. Catal. A Gen. 196 (2000) 51–66.
[30] A. Górska, K. Krawczyk, S. Jodzis, K. Schmidt-Szałowski, Fuel 90 (2011) 1946–1952.
[31] F.J. Peeters, M.C.M. Van De Sanden, Plasma Sources Sci. Technol. 24 (2015) 015016.
[32] F. Peeters, T. Butterworth, Electrical Diagnostics of Dielectric Barrier Discharges, in: A. Nikiforov, Z. Chen (Eds.), Atmos. Press. Plasma - from Diagnostics to Appl., IntechOpen, 2018, pp. 1–27.
[33] J. Kim, J. Jeoung, J. Jeon, J. Kim, Y.S. Mok, K.S. Ha, Chem. Eng. J. 377 (2019) 110896.
[34] C. De Bie, B. Verheyde, T. Martens, J. Van Dijk, S. Paulussen, A. Bogaerts, Plasma Process. Polym. 8 (2011) 1033–1058.
[35] S. Kado, K. Usasaki, Y. Sekine, K. Fujimoto, T. Nozaki, K. Okazaki, Fuel 82 (2003) 2291–2297.
[36] M. Scapinello, E. Delikonstantis, G.D. Stefanidis, Chem. Eng. J. 360 (2019) 64–74.
[37] Y. Yang, Plasma Chem. Plasma Process. 23 (2003) 283–296.
[38] P. Kasinathan, S. Park, W.C. Choi, Y.K. Hwang, J.-S. Chang, Y.K. Park, Plasma Chem. Plasma Process. 34 (2014) 1317–1330.
[39] M. Dors, H. Nowakowska, M. Jasinski, J. Mizera, Plasma Chem. Plasma Process. 34 (2014) 313–326.
[40] D. Li, V. Rohani, F. Fabry, A. Parakkal, Ramaswamy, M. Sennour, L. Fulcheri, Appl. Catal. A Gen. 588 (2019) 117269.
[41] S. Li, T. van Raak, F. Gallucci, J. Phys. D. Appl. Phys. 53 (2020) 014008.
[42] Q. Xie, S. Zhuge, X. Song, M. Li, R. Yuan, Y. Nie, J. Inf. J. Hydrogen Energy 43 (2018) 14885–14891.
[43] Z. Wang, T. Li, D. Wang, J. Zhang, H. Guo, Chunhua Xuebao, Chin. J. Catal. 36 (2015) 274–282.
[44] S. Miyagawa, K. Kotoh, S. Ogura, M. Wilde, Y. Kurokawa, K. Fukutani, N. Usami, J. Vac. Sci. Technol. A, 38 (2020) 02410.
[45] M. Kim, J. Jaekwon, J. Kim, K.-S. Ha, Appl. Catal. A Gen. 575 (2019) 214–222.
[46] E. Delikonstantis, M. Scapinello, G.D. Stefanidis, Processes. 7 (2019) 1–22.
[47] M. Młotek, J. Sentek, K. Krawczyk, K. Schmidt-Szałowski, Appl. Catal. A Gen. 366 (2009) 232–241.