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Stable High-Pressure Methane Dry Reforming Under Excess of CO₂

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Abstract: Dry reforming of methane (DRM), the conversion of carbon dioxide and methane into syngas, offers great promise for the recycling of CO₂. However, fast catalyst deactivation, especially at the industrially required high pressure, still hampers this process. Here we present a comprehensive study of DRM operation at high pressure (7–28 bars). Our results demonstrate that, under equimolar CH₄:CO₂ mixtures, coke formation is unavoidable at high pressures for all catalysts under study. However, under substoichiometric CH₄:CO₂ ratios (1:3), a stable high pressure operation can be achieved for most catalysts with no sign of deactivation for at least 60 hours at 14 bars, 800°C and 7500 h⁻¹. In addition to the enhanced stability, under these conditions, the amount of CO₂ abated per mol of CH₄ fed increases by a 50%.

Introduction

Carbon dioxide (CO₂) capture and utilization (CCU) technologies are a *conditio sine qua non* for our society to be able to deal with CO₂ emission^[1-3]. The multiple economic and technical challenges associated have sparked scientific research worldwide^[4-6]. Among the different technological solutions, dry reforming of methane (DRM), the reaction between CO₂ and CH₄ to form syngas (a mixture of CO and H₂) has gained a great deal of attention. Indeed, large amounts of CO₂ could be valorized^[7-9] to form syngas, a very versatile building block for the synthesis of chemicals and fuels via Fischer Tropsch (FTS) chemistry^[10-11]. In addition, the use of methane as co-reactant makes this technology much more attractive than alternative valorization routes that rely in i.e. H₂^[12-13].

However, despite being a promising process, the lack of a coke resistant and stable catalyst has hampered industrial application of dry reforming. A great deal of effort has been devoted to better understand the reasons behind severe coking. Nowadays it is well accepted that support defects, particle size, particle aggregation and active phase composition are the main parameters governing catalyst deactivation^[14-18]. Additionally, Nickel/Molybdenum has

been identified as the most promising non-noble system^[19-21]. Nevertheless, coke formation was still a major issue until recently Yavuz and coworkers^[22] by following a novel approach, the so called “Nanocatalyst On Single Crystal Edges” (NOSCE) technique, developed a Ni-Mo catalyst that prevented the formation of coke. The resulting material was shown to be stable for at least 850 hours at atmospheric pressure, the greatest value reached so far^[23].

Besides these remarkable advances one last requirement that could finally lead to industrial application is still needed: stability of operation at high pressures. By operating DRM at high pressure production capacity increases and, more importantly, no intermediate syngas compression, one of the most expensive unit operations in industry, is needed^[24]. To illustrate these costs constrains we performed Aspen Plus simulations of the compression process of a Syngas stream from 1 to 50 bars (see Figures S1 and S2). The equipment cost for compressing 100 ton/h of syngas, the size of a medium scale FTS plant^[25], is estimated in more than 36 million USD with an operation cost of 2240 USD per hour, with the precompression from 1 to 10 bars representing more than 85% of the total capital investment and 60% of the operational costs. Surprisingly, in spite of the obvious advantage of high-pressure operation, this is a topic that has hardly been explored experimentally due to the operational restraints^[26], as inferred from the fact that almost no publications touch upon this point.

The main issue to overcome when operating DRM at high pressure is again coke formation, highly thermodynamically favored under these conditions^[27-29]. Figure 1 and Table 1 show computed thermodynamic product distributions at different pressures. In addition to the well-known positive effect of temperature on reducing coke formation, the negative effect of pressure can be clearly observed. We can also observe that elemental carbon and water are the two main products at low temperatures where coking prevails and only above 400 °C syngas is formed. These results are well in line with previous works.^[14, 30]

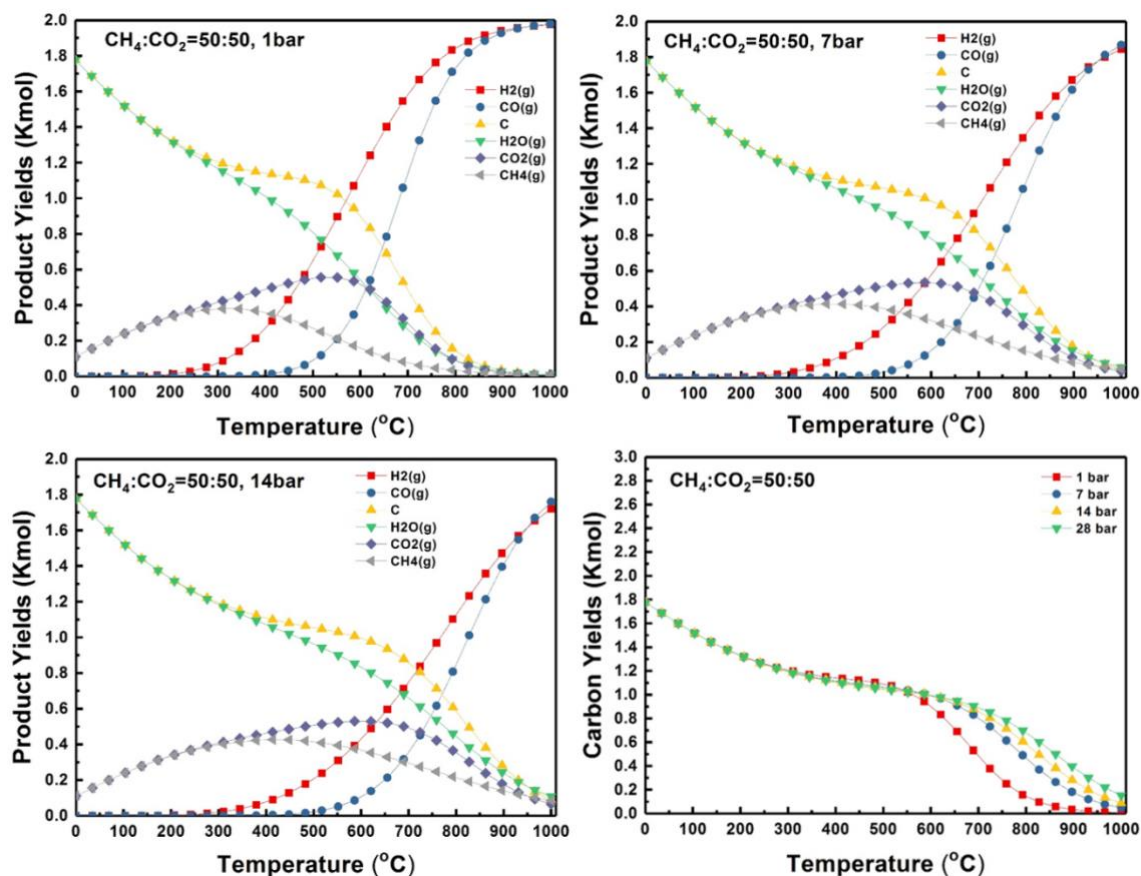


Figure 1. Thermodynamic simulations for the Dry Reforming reaction at different temperatures and pressures for a 1:1 $\text{CH}_4:\text{CO}_2$ mixture.

Table 1. Equilibrium conversions for the Dry Reforming reaction at different temperatures and pressures for a 1:1 $\text{CH}_4:\text{CO}_2$ mixture.

Conversion (%)	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
Pressure (bar)	700 °C		750 °C		800 °C	
7	76.8	53.5	81.1	61.6	88.9	71.1
14	70.5	50.7	74.6	56.4	78.7	64.6
28	64.9	49.1	68.3	52.8	71.9	58.9

Hence, in this work, by studying six different industrial catalysts under a wide range of operating conditions, we demonstrate that, under standard feed composition ($\text{CH}_4:\text{CO}_2 = 1:1$), high pressure operation leads to a strongly thermodynamic controlled reaction with very high rates of coke formation independently of the catalyst used. In contrast, with the use of substoichiometric $\text{CH}_4:\text{CO}_2$ reactant ratios (1:3), stable high pressure operation can be achieved for most catalysts. The results are rationalized as direct consequence of the Boudouard reaction that, in this particular condition of high pressure and substoichiometric feed, overcomes the increased carbon yield.

Results and Discussion

The design of the experiments (DOE) for the high-throughput screening can be found in Table 2, with a total of 15 tests performed in our high-throughput platforms for each one of the 6 catalysts. We studied the effect of temperature (700, 750 and

800°C), pressure (7, 14 and 28 bars), water co-feeding (10% vol.) and CO_2 concentration in the feed. The six industrial catalyst employed in the study were provided by Saudi Aramco and from now on will be labeled as Cat1, Cat2, Cat3, Cat4, Cat5 and Cat6. Pure magnesium oxide also was tested in all runs to ensure the absence of activity of the blank. Due to confidential agreements only basic characterization was performed. XRD analysis confirms the presence of Ni, Mo or Rh oxides supported on either Alumina, MgO or GDC (see Figure S3). Surface analysis also demonstrates that the samples display a large variety of surface area, ranging from 190 to 17 m^2/g . Altogether, this heterogeneity of the catalyst composition, in addition to the multiple conditions tested, ensures the validity of the screening.

Table 2. Screening conditions tested in the DRM reaction.

Test	$\text{CH}_4:\text{CO}_2$	P (bar)	T (°C)	GHSV (h^{-1})	Water co-feed
1	1:1	7	700	1500	no
2	1:1	14	700	1500	no
3	1:1	28	700	1500	no
4	1:1	7	750	1500	no
5	1:1	14	750	1500	no
6	1:1	28	750	1500	no
7	1:1	7	800	1500	no
8	1:1	14	800	1500	no
9	1:1	28	800	1500	no

10	1:1	14	750	1500	yes
11	1:1	14	800	1500	yes
12	1:3	14	750	1500	no
13	1:3	14	800	1500	no
14	1:3	14	800	1500	yes
15	1:3	14	800	7500	yes

The results of the first test performed at 700 °C and 7 bar are depicted in Figure 2. We can observe that: i) Cat3 and MgO (as expected) are not active at this low temperature condition; ii) only Cat4 is able to produce syngas without deactivation in the time frames studied, with a carbon balance close to 100%; iii) the rest of catalyst deactivate in a few hours and; iv) all catalysts gave similar CO₂ conversion (close to the equilibrium, see Table 1) and

only the CH₄ conversion depends on the catalyst composition. This latter fact is especially important and suggests that CO₂ conversion, unlike the CH₄ one, is strongly equilibrium limited for all catalysts at high pressure. When increasing the pressure to 14 and 28 bar (Tests 2 and 3, Figures S5 and S6 respectively) we observed that: i) deactivation rates increased rapidly with pressure, with no sample being able to sustain syngas production at 28 bars; ii) both CH₄ and CO₂ conversions are reduced upon pressure increase, in line with the data in Table1; iii) at 14 bar the reactions are not kinetically controlled anymore, with all catalysts reaching equilibrium conversion. We also need to point out that, after circa 10 hours on the reaction stream, some catalysts (Cat1, Cat2, Cat6) show slight higher CH₄ conversions than the equilibrium (see Table 1), suggesting that methane decomposition plays a key role here. This is also corroborated by the high H₂/CO ratios (above 1) of the mentioned catalysts.

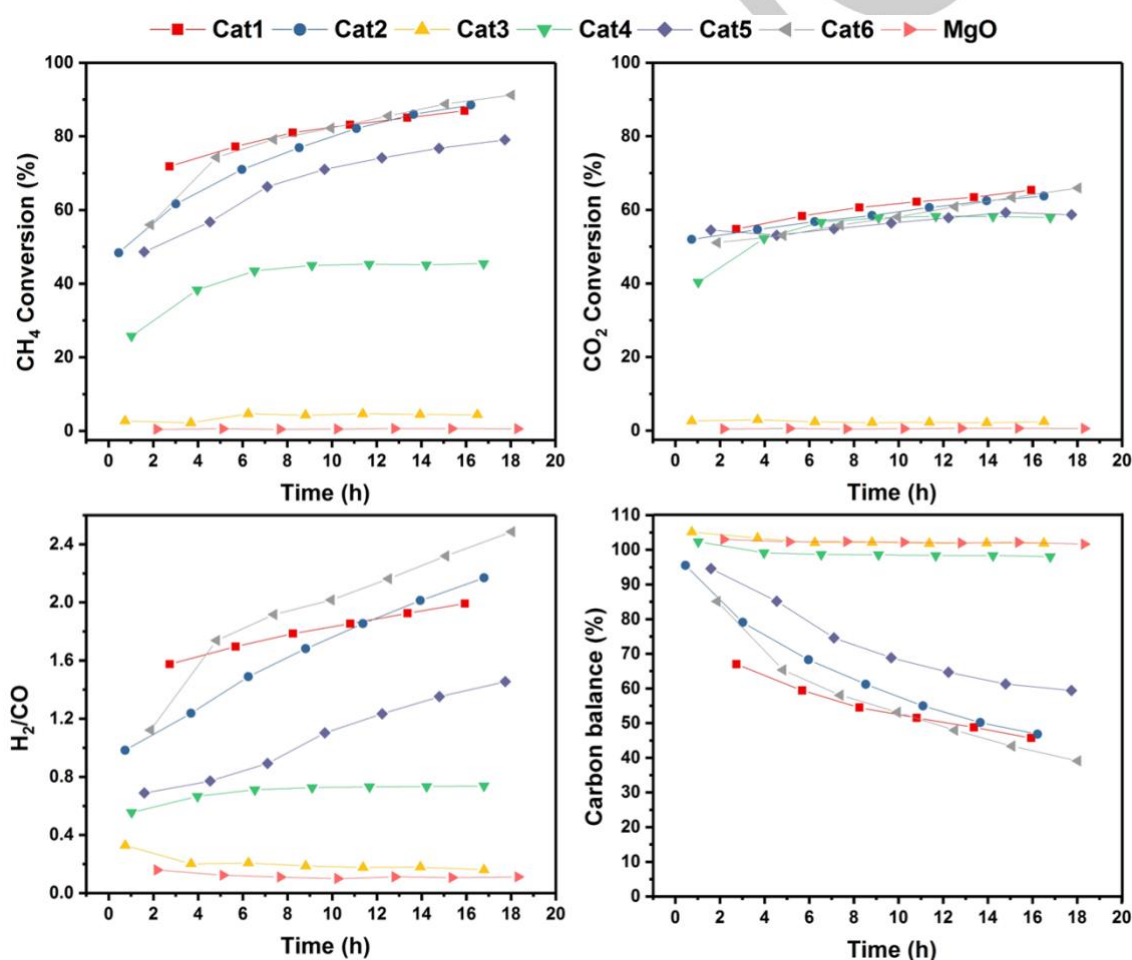


Figure 2. Catalytic performance of all samples at 700 °C and 7 bar (Test1). Reaction conditions: 700 °C, 7 bars, CH₄:CO₂ 1:1, 1500 h⁻¹.

Next, we studied the effect of temperature (700, 750 and 800 °C) at the 3 pressure ranges (7, 14 and 28 bars). The results can be found in Figures S7 to S12 (Test4 to 9 of Table 2). From these results we can observe that: i) expectedly, magnesium oxide is inert in all tests, ii) Cat3, that was inactive at 700 °C, now is active at both 750 °C and 800 °C; iii) no catalyst is able to produce syngas in sustained way at any condition, deactivating after few hours on the stream, iv) this deactivation is specially pronounced at severe conditions, like 28 bars and 800 °C, with erratic

performance of the samples, v) increasing the temperature leads to an increase of both CH₄ and CO₂ conversion (in line with the data of Table1), vi) increasing the pressure decreases the CH₄ and CO₂ conversion (again in line with the data of Table1), vii) at 750 °C and 7 and 14 bars all catalyst reach (again) the equilibrium CO₂ conversion.

In order to better observe these temperature and pressure combined effects we gathered all the results of Cat4 and plotted them in Figure 3. In line with our previous observations, it is clear

that: i) temperature increases CH_4 and CO_2 conversion with pressure having the opposite effect, ii) only at mild reaction conditions (700 °C, 7 or 14 bars) a stable syngas production is achieved in contrast with the thermodynamically suggested reduced coke formation at high temperatures (see Figure 1) and iii) high pressure and temperature strongly increase the coke formation, as derived from the low carbon balance.

To support this last statement, we performed thermogravimetric analyses of the spent catalysts after 20 hours on stream. The results are summarized in Table S2. These results confirm the high degree of coking under severe operation conditions. Under mild conditions, Cat4 seems to be the most coke resistant sample, in line with the better performance displayed in Figure 2.

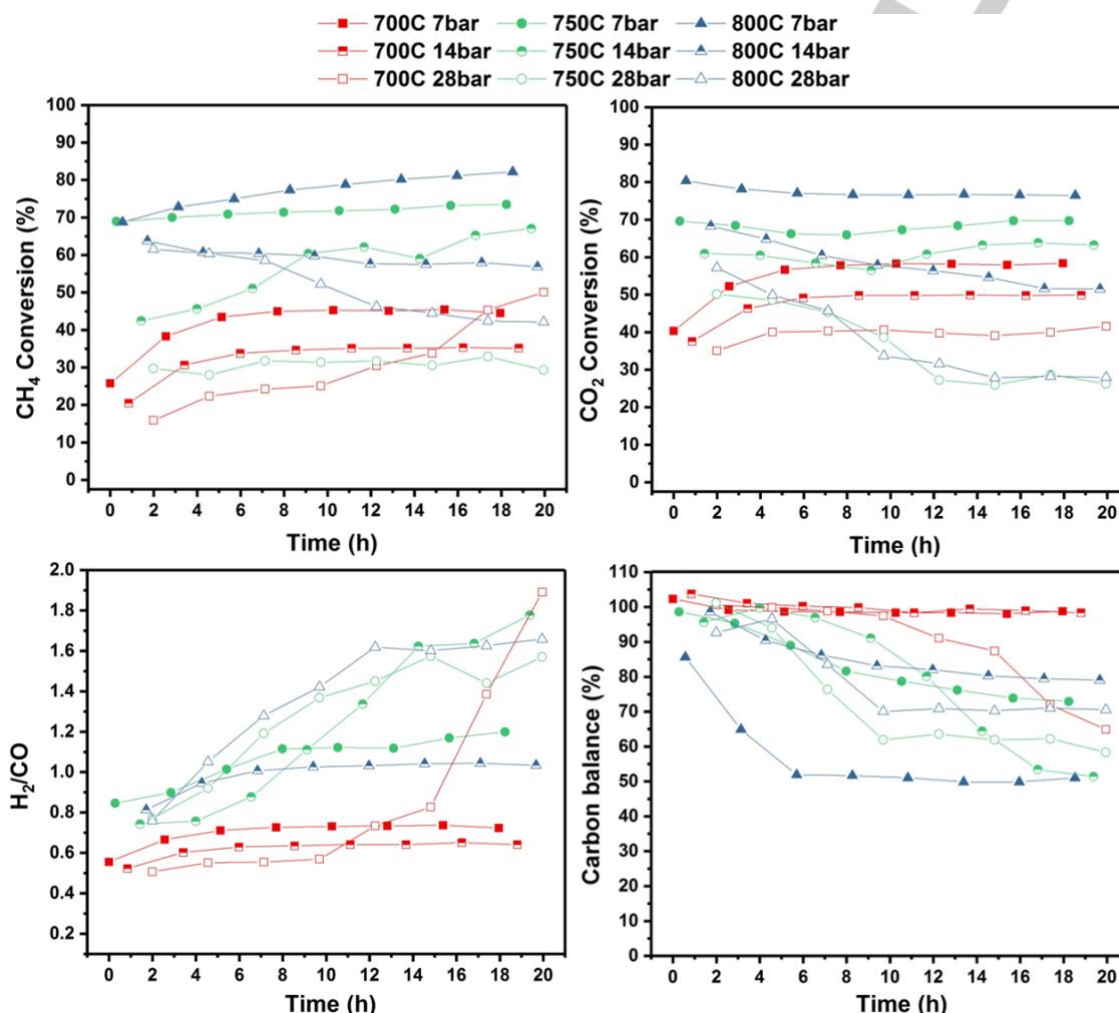


Figure 3. Effect of the reaction temperature (700, 750 and 800 °C) and pressure (7, 14 and 28 bars) on the catalytic performance of Cat4 sample, $\text{CH}_4:\text{CO}_2$ 1:1, 1500h^{-1} .

Following, we studied the effects of water co-feeding as steam reforming is well-known for reducing the coke formation and enhancing the H_2/CO ratio^[31]. The results can be found in Figures S13 and S14 (Tests10 and 11 respectively). We can observe that none of the conditions improve the stability of the catalysts despite the presence of water. Nevertheless, in line with previous reports^[32-33], the H_2/CO ratio was slightly enhanced. Next, looking for more oxidizing conditions, we varied feed composition by changing the $\text{CH}_4:\text{CO}_2$ ratios and increasing the CO_2 up to a 1:3 ratio. The results can be found in Figure S15 (750°C, Test12) and Figure S16 (800°C, Test 13). Extraordinarily, now all samples are able to sustainably produce syngas at both 750°C-800°C and 14 bars with no sign of deactivation. Moreover, all catalyst showed the same level of CH_4 conversion (~95%), CO_2 conversion (~50%), and H_2/CO ratio (~0.5) with a carbon balance close to

100%. This striking effect, already theoretically proposed by Chein and coworkers^[34], can only be explained as a result of the Boudouard reaction^[35-36] that, in these conditions, becomes the dominant step, allowing us to overcome the increased carbon yield at high pressures. To further unravel this effect we increased the reaction time to 60 hours and added extra water to the feed, trying to increase the low H_2/CO ratio (see Figure S17, Test 14). We can observe that all catalyst stay stable during the longer 60h study and, as intended, the addition of H_2O (10% vol. in the feed) slightly enhanced the H_2/CO ratio (0.6 vs 0.5).

Computed thermodynamic product distributions confirmed the reduced carbon formation in comparison with the 1:1 stoichiometric ratio (see Figure S18). However, this Boudouard-driven coke removal is (obviously) accompanied by CO formation that reduces the H_2/CO ratio, as we observed in our tests.

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Additionally, this low H_2/CO ratio also indicates an important contribution of the reverse water-gas shift reaction (RWGS: $CO_2+H_2\rightarrow CO+H_2O$), especially when considering the excess of CO_2 . Nevertheless, from a global CO_2 removal point of view, working with 1:3 $CH_4:CO_2$ ratio is advantageous as 1.5 mols of CO_2 per mol of CH_4 can be abated (for a 50% CO_2 and 100% CH_4 maximum theoretical conversion) in comparison with the ratio of 1 with the common 1:1 $CH_4:CO_2$ ratio (for a 100% CO_2 and 100% CH_4 maximum theoretical conversion). Last but not least, all catalyst seemed to be able to reach equilibrium no matter the actual catalyst composition, suggesting that, at high pressure and low space times, the DRM is under thermodynamic regime with kinetics having little to none control.

To escape from this thermodynamic control and looking for an accelerated deactivation test we further increased the space time

five times to 7500 h^{-1} GHSV while keeping the H_2O addition (see Figure 4, Test 15). We can observe that now we are finally outside thermodynamic control with catalyst composition playing a determining role, showing Cat6 the highest CO_2 conversion, Cat1 the highest H_2/CO ratio (~ 0.7) and Cat3 the lowest H_2/CO ratio (~ 0.3) respectively. This effect of Cat3 can be linked to carbon formation via CO_2 direct reduction with hydrogen. Such observation is consistent with the low CH_4 conversion observed for this catalyst in Figure 4. Nevertheless, still no deactivation was observed for any of the samples despite the higher space time. Hence, in addition to working with substoichiometric $CH_4:CO_2$ reactant ratios, high space times are also desired to escape the strong thermodynamic control at high pressure operation.

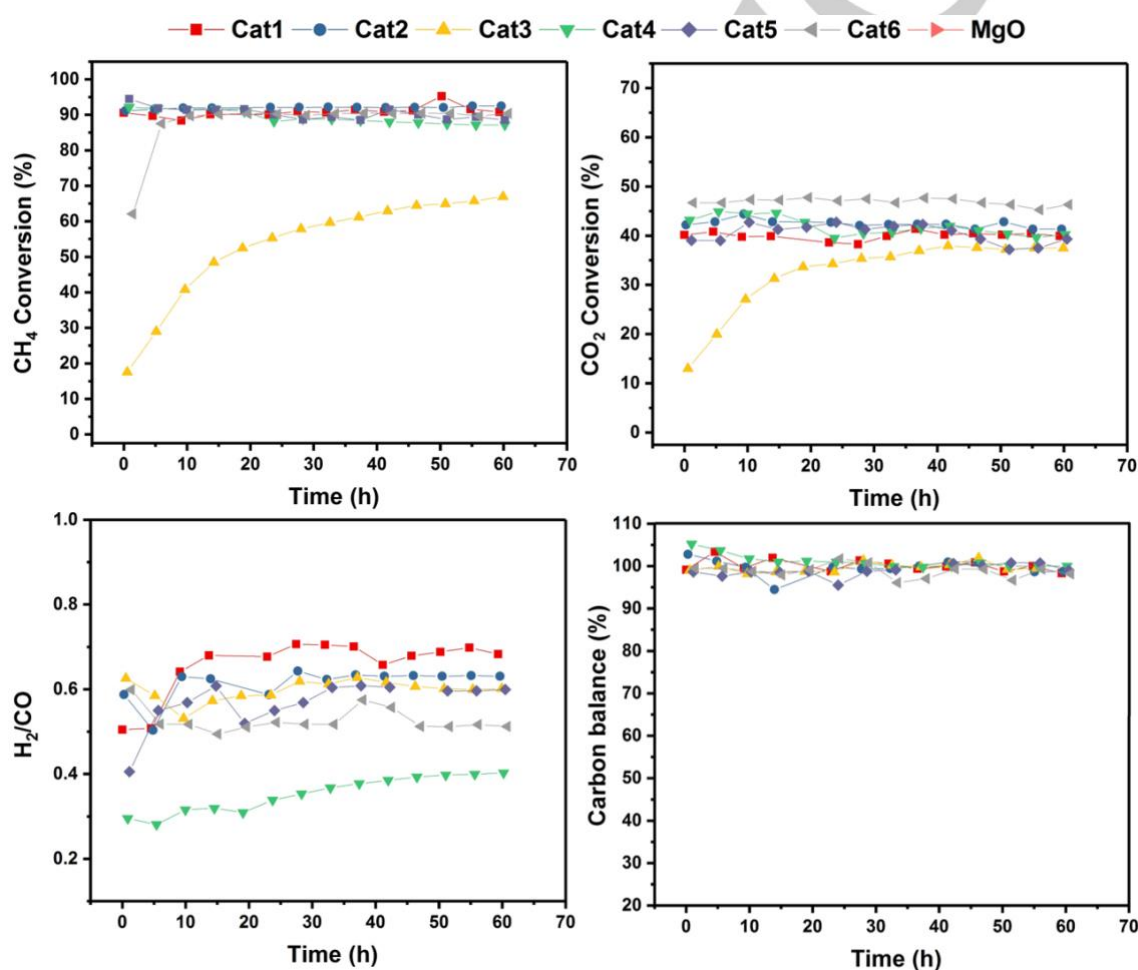


Figure 4. Catalytic performance of all samples at 800 °C and 14 bars with additional CO_2 feeding (Test15). Reaction conditions: 800 °C, 14 bars, $CH_4:CO_2$ 1:3, 10% vol. H_2O , 7500 h^{-1} .

Conclusion

In summary, our results demonstrate the enormous challenges of stable DRM performance at high pressure, as coke formation prevails no matter the catalyst employed. Only at mild conditions (low temperature and pressure) catalyst composition seems to be relevant. However, if additional CO_2 is added to the feed, a stable performance can be achieved in almost all catalytic systems thanks to the Boudouard reaction that domains the coke removal

in a strongly thermodynamic controlled system at low space times. Hence, more than developing complex catalytic systems, the feeding of additional CO_2 seems to be the easiest approach to obtain a stable syngas production at high pressures. Moreover, this extra CO_2 also increases the mols of CO_2 abated per mol of CH_4 fed by 50%. However, we also need to point out that this additional CO_2 feeding is accompanied by a decrease in the H_2/CO ratio to ~ 0.6 and, therefore, to obtain a viable high pressure DRM process, poor hydrogen syngas applications need to be

studied in parallel. We hope that these results encourage researchers to study the industrial relevant high pressure applications of DRM with the ultimate goal of a carbon neutral economy.

Experimental Section

Chemicals: Magnesium Oxide (MgO, Sigma Aldrich) was used as received.

Catalyst preparation: Catalyst samples with different compositions, based on Ni, Mo or Rh oxides supported on either Alumina, MgO or GDC (Gadolinium doped Ceria) were provided by Saudi Aramco. All samples were sieved between 150 and 250 μm before used.

Catalytic tests: Catalytic tests were executed in a 16 channel Flowrence® from Avantium. 125 μL of catalyst sample was typically used. The reactors are 300 mm long quartz tubes inserted in a furnace. The outside and inside diameters of the tubes are 3 and 2 mm, respectively. One reactor was always used without catalyst as a blank. The reactor design allows the use of quartz reactors at high pressures (see Figure S3). The 46 ml/min of mixed feed had a composition $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:1$. In addition, 4 ml/min of He were mixed with the feed as internal standard. We aimed to have 1500 h^{-1} GHSV per channel. One of the 16th channels was always used without catalyst as blank. Prior to feeding the reaction mixture all samples were pretreated in-situ with a pure H_2 atmosphere for 4 hours at 800°C. The tubes were then pressurized using a membrane pressure controller.

GC is an Agilent 7890B with two sample loops. After flushing the loops for 24 min, the content is injected. One sample loop goes to TCD channel with 2 Haysep pre-column and MS5A, where He, H_2 , CH_4 and CO are separated. Gases that have longer retention times than CO_2 on the Haysep column (Column 4 Haysep Q 0.5 m G3591-80023) are back-flushed. Further separation of permanent gases is done on another Haysep column (Column 5 Haysep Q 6 Ft G3591-80013) to separate CO_2 before going to MS5A. Another sample loop goes to an Innowax pre-column (5m, 0.20mm OD, 0.4 μm film), first 0.5 min of the method the gases coming from pre-column are sent to Gaspro column (Gaspro 30M, 0.32 mm OD) followed by FID. After 0.5 min, valve is switched and gases are sent to Innowax column (45 m, 0.2 mm OD, 0.4 μm) followed by FID. Gaspro column separates C_1 - C_8 , paraffins and olefins. Innowax separates larger hydrocarbons ($>\text{C}_9$) and aromatics BTX and C_9+ aromatics. No C_2+ products were detected in any of the performed tests. Conversions (X, %) and carbon balance are defined as follows:

$$\text{Conv}_{\text{CO}_2} (\%) = \frac{\text{CO}_{2,\text{in}}/\text{He}_{\text{in}} - \text{CO}_{2,\text{out}}/\text{He}_{\text{out}}}{\text{CO}_{2,\text{in}}/\text{He}_{\text{in}}} \times 100$$

$$\text{Conv}_{\text{CH}_4} (\%) = \frac{\text{CH}_{4,\text{in}}/\text{He}_{\text{in}} - \text{CH}_{4,\text{out}}/\text{He}_{\text{out}}}{\text{CH}_{4,\text{in}}/\text{He}_{\text{in}}} \times 100$$

$$\text{C}_{\text{balance}} (\%) = \frac{\sum \text{C}_{\text{out}}/\text{He}_{\text{out}}}{\sum \text{C}_{\text{in}}/\text{He}_{\text{in}}} \times 100$$

where C_{in} and C_{out} , are the concentrations determined by GC analysis in the blank and in the reactor outlet respectively.

Thermogravimetric analysis (TGA): TGA Analysis was performed with a METTLER TOLEDO TGA/DSC 1 instrument. Approximately 10 mg of sample was weighed inside an alumina crucible. In order to remove any volatile species, samples were heated from RT to 200 °C with a ramp of 10 Cmin^{-1} under a flow of N_2 (50 mLmin^{-1}) followed by an isothermal step of 60 min. The temperature was again increased up to 800 °C with a ramp of 10 Cmin^{-1} in order to pyrolyze the coked samples. The sample was kept at 800 °C under a flow of N_2 (50 mLmin^{-1}) for 30 min before switching the gas to Air (50 mLmin^{-1}) in order to oxidized the coked sample.

X-Ray diffraction (XRD): XRD analysis was performed on BRUKER D8 ADVANCE instrument from 5 to 90 2 theta degrees and an increment of 0.01 degrees.

Nitrogen adsorption: Nitrogen physisorption measurements were performed on an ASAP2420 MICROMERITICS instrument. Prior to obtaining the isotherm the samples were dried under vacuum with a ramp rate of 10 Cmin^{-1} up to 90 °C for 60 min followed by a final heat treatment at 300 C° for 720 min. After weighing the dried samples they were additionally degassed under vacuum at 90 °C for 120 min at the analysis ports of the instrument prior to acquirement of isotherm by stepwise dosing of N_2 at 77 K. As last the correct free space values were obtained by performing additionally 1 point measurement using N_2 and exposing the sample to Helium.

Process simulations and thermodynamic calculations: Process simulations were carried out with steady-state simulation models developed in Aspen Plus V8.8 software. Economic analysis was carried out with the Economics Solver extension of Aspen Plus. The selected property method was Redlich-Kwong-Soave. The Wegstein method was used for flowsheet convergence with a mass balance closure of the system better than 0.0001. The total flow is 100 tons/hour of Syngas ($\text{CO}:\text{H}_2$ 1:1) with a target pressure of 50 bars. The feed stream was compressed by 4 four isentropic compressors (C1 to C4 in FigureS1) with intercooling heat exchangers (HX1 to HX3 in Figure S1) to cool down the pressurized streams. Thermodynamic equilibrium was calculated by using HSC 5.1 chemistry software with a method of Gibbs free energy minimization. Same feed compositions of reactants as the experimental conditions were used and calculated with varying pressures and temperatures. In order to investigate carbon formation, solid carbon was considered to be one of the products as well as gaseous H_2 , CO, and H_2O . Thermodynamic equilibrium results were used as reference data to compare the experimental results.

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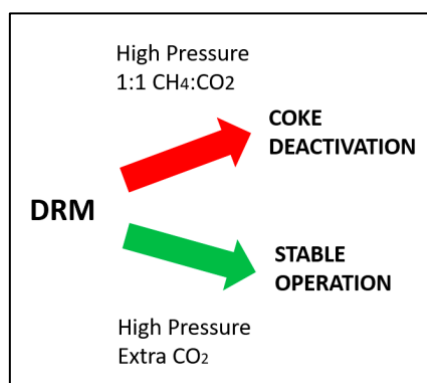
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Keywords: Dry Reforming • CO_2 • CH_4 • Hydrogen • Syngas • Pressure

- [1] N. Mac Dowell, P. S. Fennell, N. Shah, G. C. Maitland, *Nat Clim Change* **2017**, 7, 243-249.
- [2] C. F. Shih, T. Zhang, J. H. Li, C. L. Bai, *Joule* **2018**, 2, 1925-1949.
- [3] R. Dittmeyer, M. Klumpp, P. Kant, G. Ozin, *Nature Communications* **2019**, 10, 1818.
- [4] A. Alvarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem Rev* **2017**, 117, 9804-9838.
- [5] G. Centi, E. A. Quadrelli, S. Perathoner, *Energ Environ Sci* **2013**, 6, 1711-1731.
- [6] A. Dokania, A. Ramirez, A. Bavykina, J. Gascon, *Acs Energy Lett* **2019**, 4, 167-176.
- [7] C. O. Hawk, P. L. Golden, H. H. Storch, A. C. Fieldner, *Ind Eng Chem* **1932**, 24, 23-27.
- [8] N. A. K. Aramouni, J. G. Touma, B. Abu Tarboush, J. Zeaiter, M. N. Ahmad, *Renew Sust Energ Rev* **2018**, 82, 2570-2585.
- [9] J. M. Lavoie, *Front Chem* **2014**, 2.
- [10] V. P. Santos, T. A. Wezendonk, J. J. D. Jaen, A. I. Dugulan, M. A. Nasalevich, H. U. Islam, A. Chojecki, S. Sartipi, X. Sun, A. A. Hakeem, A. C. J. Koeken, M. Ruitenbeek, T. Davidian, G. R. Meima, G. Sankar, F. Kapteijn, M. Makkee, J. Gascon, *Nature Communications* **2015**, 6.
- [11] G. P. Van der Laan, A. A. C. M. Beenackers, *Catal Rev* **1999**, 41, 255-318.

- [12] A. Gonzalez-Garay, M. S. Frei, A. Al-Qahtani, C. Mondelli, G. Guillen-Gosalbez, J. Perez-Ramirez, *Energy Environ Sci* **2019**, *12*, 3425-3436.
- [13] G. Glenk, S. Reichelstein, *Nat Energy* **2019**, *4*, 216-222.
- [14] S. Arora, R. Prasad, *Rsc Adv* **2016**, *6*, 108668-108688.
- [15] O. Muraza, A. Galadima, *Int J Energy Res* **2015**, *39*, 1196-1216.
- [16] P. Djinovic, I. G. O. Crnivec, B. Erjavec, A. Pintar, *Appl Catal B-Environ* **2012**, *125*, 259-270.
- [17] J. M. Ginsburg, J. Pina, T. El Solh, H. I. de Lasa, *Ind Eng Chem Res* **2005**, *44*, 4846-4854.
- [18] L. Guzzi, G. Stefler, O. Geszti, I. Sajo, Z. Paszti, A. Tompos, Z. Schay, *Appl Catal a-Gen* **2010**, *375*, 236-246.
- [19] L. Yao, M. E. Galvez, C. W. Hu, P. Da Costa, *Int J Hydrogen Energy* **2017**, *42*, 23500-23507.
- [20] Z. W. Yao, J. Jiang, Y. Zhao, F. B. Luan, J. Zhu, Y. Shi, H. F. Gao, H. Y. Wang, *Rsc Adv* **2016**, *6*, 19944-19951.
- [21] C. Shi, S. H. Zhang, X. S. Li, A. J. Zhang, M. Shi, Y. J. Zhu, J. S. Qiu, C. T. Au, *Catal Today* **2014**, *233*, 46-52.
- [22] J. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz, *Science* **2020**, *367*, 777-+.
- [23] A. Ramirez, J. Gascon, *Joule* **2020**, *4*, 714-716.
- [24] S. S. Penner, *Energy* **2006**, *31*, 33-43.
- [25] H. Er-rbib, C. Bouallou, F. Werkoff, *Energy Procedia* **2012**, *29*, 156-165.
- [26] L. C. S. Kahle, T. Roussiere, L. Maier, K. H. Delgado, G. Wasserschaff, S. A. Schunk, O. Deutschmann, *Ind Eng Chem Res* **2013**, *52*, 14727-14727.
- [27] R. Y. Chein, Y. C. Chen, C. T. Yu, J. N. Chung, *J Nat Gas Sci Eng* **2015**, *26*, 617-629.
- [28] L. A. Schulz, L. C. S. Kahle, K. H. Delgado, S. A. Schunk, A. Jentys, O. Deutschmann, J. A. Lercher, *Appl Catal a-Gen* **2015**, *504*, 599-607.
- [29] I. Khan, A. Ramirez, G. Shterk, L. Garzon-Tovar, J. Gascon, *Catalysts* **2020**, *10*.
- [30] D. Pakhare, C. Shaw, D. Haynes, D. Shekhawat, J. Spivey, *Journal of CO2 Utilization* **2013**, *1*, 37-42.
- [31] P. Gangadharan, K. C. Kanchi, H. H. Lou, *Chem Eng Res Des* **2012**, *90*, 1956-1968.
- [32] W. J. Jang, D. W. Jeong, J. O. Shim, H. M. Kim, H. S. Roh, I. H. Son, S. J. Lee, *Appl Energy* **2016**, *173*, 80-91.
- [33] K. Y. Koo, H. S. Roh, U. H. Jung, D. J. Seo, Y. S. Seo, W. L. Yoon, *Catal Today* **2009**, *146*, 166-171.
- [34] R. Y. Chein, W. H. Hsu, C. T. Yu, *Int J Hydrogen Energy* **2017**, *42*, 14485-14500.
- [35] J. W. Snoeck, G. F. Froment, M. Fowles, *Ind Eng Chem Res* **2002**, *41*, 4252-4265.
- [36] B. P. Jalan, Y. K. Rao, *Carbon* **1978**, *16*, 175-184.

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Towards High-Pressure Methane Dry Reforming. The conversion of both CO₂ and CH₄ greenhouse gases via dry methane reforming (DRM) could provide an environmentally friendly route for the synthesis of valuable chemicals. However, to achieve the final industrial application research at high pressure feeds is still required. In this work we have explored the DRM reaction at high pressure via a comprehensive high-throughput screening on 6 different industrial catalysts. Our results demonstrate the enormous challenges of stable DRM performance under these high pressure conditions. Nevertheless, we have also found that with the use of substoichiometric CH₄:CO₂ reactant ratios (i.e. 1:3) stable high pressure operation can be achieved for most catalysts with no sign of deactivation.

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