Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 89 (2004) 21–25
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Plasma catalytic conversion of methane into syngas: the combined effect of discharge activation and catalysis

M. Heintze*, B. Pietruszka

Institute of Low Temperature Plasma Physics (INP), Friedrich-Ludwig-Jahn-Str. 19, 17489 Greifswald, Germany

Abstract

In the current study we investigate the combined operation of a dielectric barrier discharge and an α-alumina supported Ni catalyst in the partial oxidation of methane. In order to separate the effects of plasma activation from catalytic processes, the study includes both purely catalytic and plasma-activated operation of the reactor. Whereas the catalyst alone is only active above 300 °C, plasma induced partial oxidation of methane is observed in the entire temperature range investigated (100–400 °C). By comparing the reaction over the Ni catalyst in different oxidation states with the catalyst support only, conclusions are drawn regarding surface and gas phase processes.

Keywords: Synthesis gas; Partial oxidation; Methane; Plasma

1. Introduction

The conversion of natural gas into hydrogen, synthesis gas (syngas) or liquid hydrocarbons is currently receiving increasing attention. This is in part motivated by the need to utilize natural gas from remote sources and also by novel fuel cell applications. As an alternative method to conventional chemical or catalytic processes, plasmas are studied. However, still a prohibitively high amount of energy is required for plasma excitation.

The catalysts commonly used for syngas production are based on transition metals (e.g. Ni, Rh, Pt, Ir) supported on metal oxides, such as Al_2O_3, CeO_2, MgO, TiO_2 or rare-earth oxides [1–10]. Among those, nickel-based catalysts have been most widely investigated due to their high activity and low cost [6–10].

Various non-thermal plasmas (dielectric barrier discharge (DBD), corona, gliding arc and microwave plasmas) have been studied for methane conversion into higher hydrocarbons [11], dry reforming in combination with catalysts [12–15] or acetylene production [16,17].

A catalyst placed in the plasma zone can influence the plasma properties, e.g. due to the presence of conductive surfaces, in the case of metallic catalysts. The catalyst can also change the reaction products due to surface reactions [13]. On the other hand, the plasma can influence the catalyst properties; it causes heating of the catalyst, and therefore can induce desorption of surface species. A synergy between catalysis and plasma is achieved if plasma–catalyst interactions lead to improved reagent conversions or higher selectivity to the desired products as compared to the purely plasma-chemical or catalytic process.

As reported by Liu et al. [11], the catalytic reactions occurring in the presence of a gas discharge depend on the gas temperature. The most significant influence of the plasma was observed at low temperatures, where the catalysts were not active. At higher temperatures, the catalysts became active, however, the plasma catalytic effect was still observed.

The presence of a catalyst influences the CO_2 and CH_4 conversion in methane dry reforming in a DBD [12,13]. Various catalysts were investigated, in the temperature range between 40 and 230 °C. Over Ni and Ni–Ca, carbon dioxide was decomposed to CO and O_2. A Rh catalyst showed surprisingly low activity in these studies, although it is known to be a good catalyst for methane decomposition [2–4]. It was proposed that CO and O_2 produced in the discharge react over Rh to form CO_2. The CH_4 decomposition and selectivity to H_2 showed no differences between the Ni-containing catalysts and pure alumina.

The present paper reports recent results on the combination of plasma and catalysis for methane partial oxidation to CO and H_2. The catalyst employed in the experiments was Ni supported on α-Al_2O_3. The methane and oxygen conversion and the selectivity towards reaction products were

* Corresponding author. Tel.: +49-3834-554413; fax: +49-3834-554301.
E-mail address: heintze@inp-greifswald.de (M. Heintze).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.11.006

determined both in the purely thermal catalytic process and in the presence of the plasma. The results obtained with catalyst, in different oxidation states, were compared to results achieved without catalyst, over the Al_2O_3 support, providing information on gas-phase and surface processes.

2. Experimental

The DBD reactor [18] consists of two coaxial quartz tubes of 20 and 15 mm outer diameter. The discharge gap is 1.5 mm and the length of the discharge zone is 10 cm, resulting in a reaction volume of approximately 7 cm^3. As high voltage electrode a metal coating on the inside of the inner tube was used. The outer electrode is a metal spiral, wound around the outer tube. This metal spiral provides also the heating of the reactor. The discharge is operated with a.c. voltage of maximum 10 kV (r.m.s.) at frequencies of 25–40 kHz. The discharge power was calculated from the time-averaged product of the discharge voltage and current. The reactor temperature was measured at the outer tube by a thermocouple.

A commercial Ni/α-Al_2O_3 catalyst (Süd-Chemie G90B) was used, with specific surface area of 6 m^2/g, grain size 0.71–1.00 mm, containing about 10% of Ni as NiO. The reducibility and oxidability of the catalyst were measured by temperature programmed reduction/oxidation (TPR/O) on samples of approximately 240 mg, in 5% H_2 in Ar and 5% O_2 in He, respectively. During TPR/O, the gas flow rate was 20 sccm; the sample was heated from 60 to 800 °C at 10 K min^{-1}. The oxidation and reduction measurements were repeated a few times to investigate the stability.

Plasma catalytic measurements were carried out using 2 g of catalyst placed at the outlet side of the discharge zone, filling about one-third of the discharge volume. The catalyst was first calcinated in air at 700 °C for 4 h. For the plasma catalytic experiments, samples were used as calcinated (NiO/α-Al_2O_3) and after reduction (Ni/α-Al_2O_3). The reduction was carried out with 6.7% H_2 in Ar at 150 sccm, from 200 to 450 °C at 5 K min^{-1} and kept at 450 °C for 1 h.

The catalytic tests were conducted at temperatures up to 400 °C using air as oxidant. The total gas flow rate was in the range 160–480 sccm, with CH_4:O_2 = 2:1. A small amount of argon (6.6 vol.%) was added to monitor the total volume flow rate at the reactor outlet and the volume variations during the reaction. The products were analyzed on-line by non-dispersive infrared spectrometry (NDIR), mass spectrometry (MS) and gas chromatography (GC).

3. Results

3.1. Temperature programmed reduction and oxidation (TPR/O) measurements

The catalyst showed very good stability with respect to its reducibility and oxidability. During re-oxidation and re-reduction to 800 °C, no changes in the peak shapes were observed in subsequent runs. Always 100% of the nickel in the sample was converted.

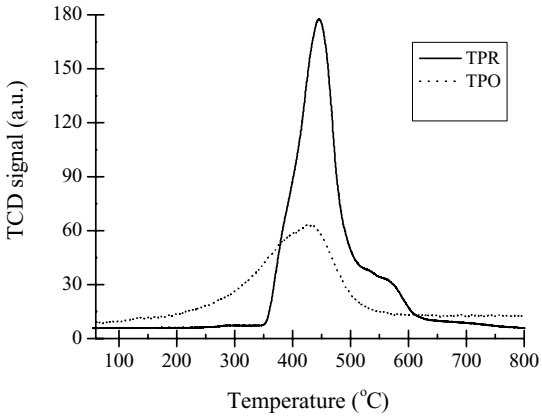

Fig. 1. TPR profile of NiO/α-Al_2O_3 (solid line) and TPO profile of Ni/α-Al_2O_3 (dotted line).

Fig. 1 shows the TPR and TPO profiles. The reduction and oxidation profiles show a maximum at approximately 440 °C. The Ni/α-Al_2O_3 starts to be oxidized above 200 °C, while reduction of NiO/α-Al_2O_3 starts above 300 °C. This temperature range is typical for supported NiO, as a result of considerable interaction between nickel ions and the support [19]. For unsupported NiO the temperature of reduction is lower, with a maximum at about 320 °C [20], while reduction of NiO/α-Al_2O_3 was reported to be not complete even up to 700 °C [21].

3.2. Plasma chemical POM over nickel catalyst and catalyst support

The main products of the plasma catalyzed partial oxidation of methane were CO, CO_2, H_2O and H_2. Traces of methanol, ethanol and C_2–C_4 hydrocarbons were detected as by-products, at concentrations below 0.5%. Carbon and carbonaceous deposit was observed on the reactor walls after the experiments.

In Table 1 the methane and oxygen conversion over α-Al_2O_3, Ni/α-Al_2O_3 and NiO/α-Al_2O_3 without plasma (P = 0 W) and with plasma, with the power set to P = 20 W are summarized for temperatures between 100 and 400 °C. No methane and oxygen conversion was observed over α-Al_2O_3 in a purely thermal process. Conversion of methane and oxygen starts in the thermal catalytic reaction without discharge at 300 °C over Ni and at 400 °C over NiO. This is consistent with the result shown in Fig. 1, where the on-set of Ni oxidation is lower than that of NiO reduction: catalytic activity requires the co-existence of oxidized an reduced Ni sites on the surface. Operating the discharge induces POM over all the materials in the temperature range investigated. The methane conversion is nearly independent of temperature and the material in the discharge, whereas

Table 1
Methane and oxygen conversion over Ni and NiO on α-Al_2O_3 as well as plain Al_2O_3 catalyst support (thermal versus plasma-assisted operation at 20 W plasma power)

Sample	Power (W)	CH_4 conversion (%)				O_2 conversion (%)			
		100 °C	200 °C	300 °C	400 °C	100 °C	200 °C	300 °C	400 °C
Al_2O_3	0	0	0	0	0	0	0	0	0
Ni/Al_2O_3	0	0	0	7	12	0	0	12	45
NiO/Al_2O_3	0	0	0	0	3	0	0	0	12
Al_2O_3	20	20	23	26	29	50	55	67	77
Ni/Al_2O_3	20	19	22	25	27	48	55	85	95
NiO/Al_2O_3	20	18	22	25	28	46	54	78	85

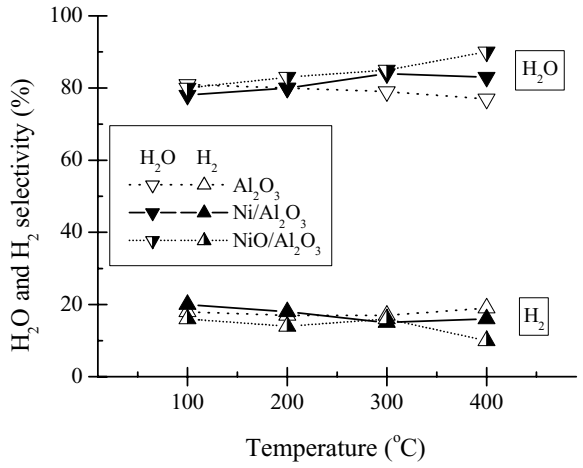

Fig. 2. Selectivity to H_2O and H_2 over α-Al_2O_3, $Ni/α$-Al_2O_3 and $NiO/α$-Al_2O_3 in the presence of the discharge (20 W plasma power, 160 sccm total flow).

the oxygen conversion is enhanced over NiO and even more over Ni at 300 °C, as compared to the α-Al_2O_3 support.

In Fig. 2 the selectivity to H_2O and H_2 and in Fig. 3 the selectivity to CO and CO_2 are shown in the presence of discharge over α-Al_2O_3, $Ni/α$-Al_2O_3 and $NiO/α$-Al_2O_3. The selectivity to H_2O and H_2 is almost independent of temperature and the material in the discharge zone. The selectivity to CO and CO_2 is constant over all the materials up to 200 °C. The selectivity to CO drops drastically at 300 °C together with an increase in selectivity to CO_2 over the Ni catalyst, and at 400 °C over NiO. Over α-Al_2O_3 the selectivity to CO does not change much and only a slight increase in selectivity to CO_2 is observed. The comparison with purely thermal conditions ($P = 0$ W) indicates that oxygen is consumed by CO oxidation in a catalytic reaction. At lower temperature, where Ni and NiO cannot be reduced or oxidized, only gas phase processes are taking place, i.e. the Ni and NiO catalysts were not active.

3.3. Efficiency of syngas production

The methane and oxygen conversion in the DBD in the absence of a catalyst is essentially determined by the specific input energy (SIE), defined as the ratio of the plasma power to the total flow rate, whereas the selectivity to CO and H_2 remains independent of the SIE [18]. An important question is the effectiveness for syngas production of the plasma-assisted process. The energy required for methane and oxygen conversion is shown in Figs. 4 and 5, respec-

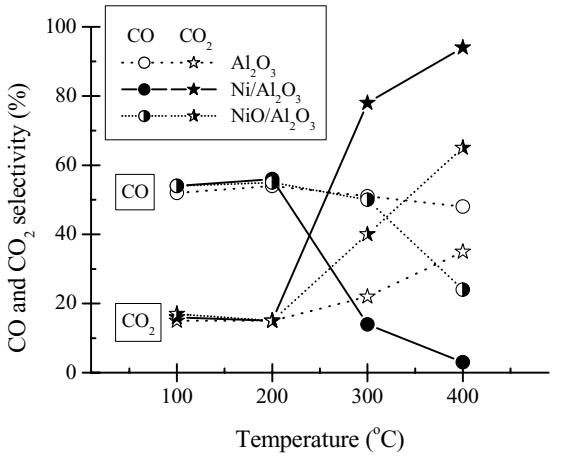

Fig. 3. Selectivity to CO and CO_2 over α-Al_2O_3, $Ni/α$-Al_2O_3 and $NiO/α$-Al_2O_3 in the presence of the discharge (20 W plasma power, 160 sccm total flow).

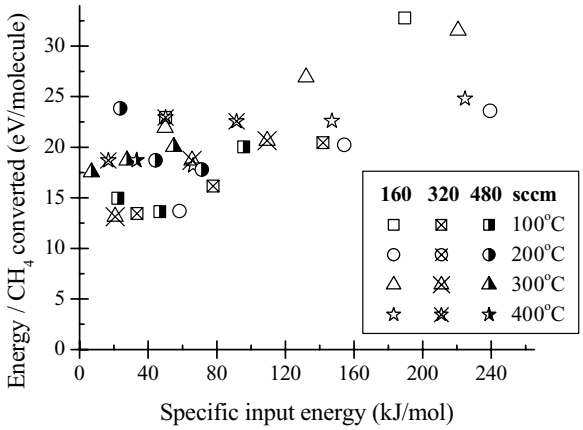

Fig. 4. Energy requirement per converted methane molecule versus specific input energy at temperatures between 100 and 400 °C and different flows over 2 g of α-Al_2O_3 in the discharge zone.

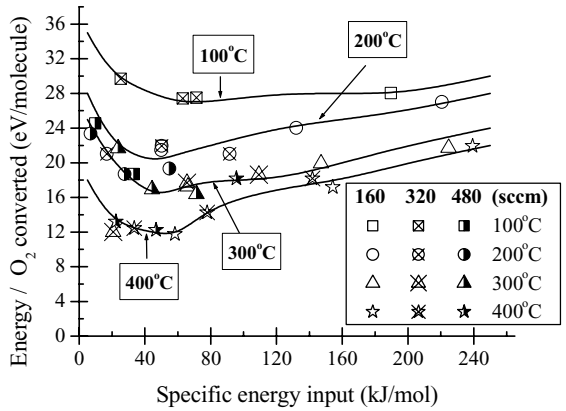

Fig. 5. Energy requirement per converted oxygen molecule versus specific input energy, conditions as in Fig. 4.

tively. The energy required for syngas production ($CO + H_2$) is plotted in Fig. 6.

The energy requirement for methane conversion is about 16 eV/molecule (1.5 MJ/mol) at low SIE, and increases slightly with SIE, but is essentially independent of temperature. The energy requirement for oxygen conversion is shows a shallow minimum around SIE = 40 kJ/mol however it decreases at higher temperatures.

As shown in Fig. 6, the energy required for CO and H_2 production shows a minimum at an SIE of about 20–30 kJ/mol and increases slightly for higher SIE. The temperature dependence is the same as for the energy requirement for oxygen conversion. The temperature increase promotes the oxygen conversion and decreases the energy requirement for syngas formation.

The relatively high energy requirement per molecule of converted CH_4 and O_2 indicates that the plasma power does not only excite the reacting gases, but that competing dissipation paths could be present, such as the excitation of nitrogen which does not participate in the reaction.

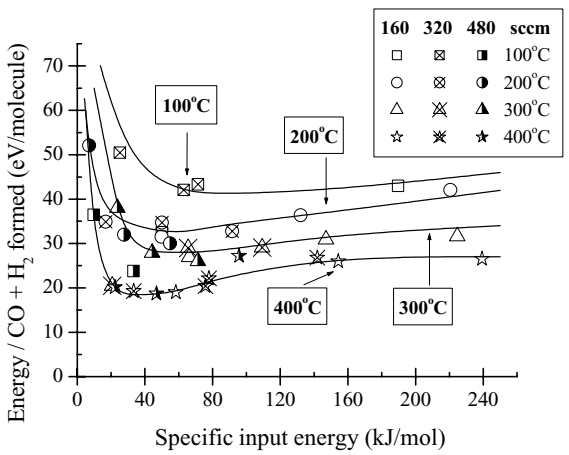

Fig. 6. Energy requirement for syngas production, i.e. per molecule of $H_2 + CO$, versus specific input energy, conditions as in Fig. 4.

4. Discussion

The results presented show that the activity of the Ni-catalyst depends on its ability to be reduced and oxidized. The onset of activity without plasma (Table 1) correlates closely with the TPR/O profiles (Fig. 1). Only when NiO is partially reduced or Ni is partially oxidized, respectively, catalytic methane activation is observed.

The plasma on the other hand allows to partially oxidize methane independent of temperature in the entire range investigated. This is due to electron impact induced dissociation of the reactants. Over the catalytically inert α-alumina, both the conversion of reactants and the product selectivities are almost independent of temperature, underlining the basically non-thermal character of the plasma. The Ni-catalyst has in this case the effect of leading to the oxidation of $CO–CO_2$. Also this surface reaction sets in at temperatures where the TPR/O profiles show the onset of activity. The bulk NiO cannot oxidize $CO–CO_2$ up to 300 °C, but when it becomes reduced in the reagents mixture and the presence of the discharge at 400 °C, oxidation of $CO–CO_2$ is observed. The metallic nickel surface is first partially oxidized and then causes oxidation of $CO–CO_2$. In the presence of a discharge the process is intensified, but not at temperatures below 200 °C, where the catalyst is not active.

Under thermal conditions the gas phase reaction between CH_4 and O_2 does not occur at 700 °C and on oxidized Ni sites (NiO) CH_4 is decomposed non-selectively to CO_2 and H_2O. Reversibly adsorbed oxygen and active metallic Ni sites are needed for CH_4 decomposition into H_2 and CO [6,7]. The coexistence of metallic Ni and NiO_x species [22] on the catalyst surface is responsible for the activation of methane to syngas. Such mechanism was also reported over a Rh catalyst [3].

As reported by Caldwell et al. [23] in plasma induced partial oxidation of methane to synthesis gas without a catalyst in the discharge, a CO/CO_2 ratio of about 9 was obtained, indicating that plasma promotes CO formation rather than its further oxidation to CO_2. Such high CO formation was also observed in the methane–oxygen mixture in a corona discharge over oxide catalysts and zeolites [11] and in dry reforming of methane, as long as the catalyst was inactive [13].

On the other hand, the rather stable selectivity values to H_2O and H_2 indicate that the surface does not play any role in H_2 oxidation or H_2O decomposition reactions. However, a much higher selectivity to H_2 was only achieved if the oxygen conversion approached 100%, e.g. at sufficiently high plasma power or reactor temperatures over the nickel catalyst [24].

5. Conclusions

The main products of plasma induced methane–oxygen reaction are CO and H_2O, as long as the oxygen conversion is not complete. At lower temperatures (up to 200 °C) the

discharge determines the partial oxidation of methane and the presence of α-Al_2O_3, Ni/α-Al_2O_3 or NiO/α-Al_2O_3 has no influence on the conversion and product selectivity. At this temperature the plasma gas phase processes dominate. At higher temperatures the presence of metallic Ni or NiO supported on α-alumina promotes oxidation of CO to CO_2. The selectivity to H_2O and H_2 remains almost unchanged as long as full oxygen conversion is not achieved, indicating that it is determined by gas phase reactions.

Acknowledgements

This research was supported by the E.U. (contract number ICA2-CT-2000-10004).

References

[1] K. Nakagawa, N. Ikenaga, T. Suzuki, T. Kobayashi, M. Haruta, Appl. Catal. A 169 (1998) 281.
[2] H.H. Hofstad, J.H.B.J. Hoebink, A. Holmen, G.B. Marin, Catal. Today 40 (1998) 157.
[3] B. Pietruszka, M. Najbar, L. Lityńska-Dobrzyńska, E. Bielańska, M. Zimowska, J. Camra, Stud. Surf. Sci. Catal. 36 (2001) 471.
[4] L. Basini, A. Guarinoni, A. Aragno, J. Catal. 190 (2000) 284.
[5] P. Pantu, G.R. Gavalas, Appl. Catal. A 223 (2002) 253.
[6] Ch. Li, Ch. Yu, S. Shen, Catal. Lett. 67 (2000) 139.
[7] R. Jin, Y. Chen, W. Li, W. Cui, Y. Ji, Ch. Yu, Y. Jiang, Appl. Catal. A 121 (2000) 71.
[8] A. Djaidja, A. Barama, M.M. Bettahar, Catal. Today 212 (2000) 1.
[9] T. Shishido, M. Sukenobu, H. Morioka, M. Knodo, Y. Wang, K. Takaki, K. Takehira, Appl. Catal. A 223 (2002) 35.
[10] Z.-W. Liu, K.-W. Jun, H.-S. Roh, S.-Ch. Baek, S.-E. Park, J. Mol. Catal. A 189 (2002) 283.
[11] Ch. Liu, A. Marafee, R.G. Mallinson, L. Lobban, Appl. Catal. 164 (1997) 21.
[12] M. Kraus, B. Eliasson, U. Kogelschatz, A. Wokaun, Phys. Chem. Chem. Phys. 3 (2001) 294.
[13] M. Kraus, Ph.D. Thesis, Swiss Federal Institute of Technology, Zurich, 2001.
[14] K. Zhang, B. Eliasson, U. Kogelschatz, Ind. Eng. Chem. Res. 41 (2002) 1462.
[15] A. Czernichowski, Oil Gas Sci. Technol. Rev. IFP 56 (2001) 181.
[16] M. Heintze, M. Magureanu, J. Appl. Phys. 92 (2002) 2276.
[17] K. Schmidt-Szałowski, K. Krawczyk, J. Ruszinak, in: A. Bouchoule, J.M. Pouvesle, A.L. Thomann, J.M. Bauchire, E. Robert (Eds.), Proceedings of the 15th International Symposium on Plasma Chemistry, Orleans, France, 2001, p. 2933.
[18] B. Pietruszka, K. Anklam, M. Heintze, Appl. Catal. A, in press.
[19] M. Lo Jacono, M. Schiavello, A. Cimino, J. Phys. Chem. 75 (1971) 1044.
[20] S.D. Robertson, B.D. McNicol, J.H. de Baas, S.C. Kloet, J. Catal. 37 (1975) 424.
[21] J.R. Ross, M.C.F. Steel, A. Zeini-Isfahani, J. Catal. 52 (1978) 280.
[22] Y. Lu, J. Xue, C.C. Yu, S.K. Shen, Appl. Catal. A 174 (1998) 121.
[23] T.A. Caldwell, H. Le, L.L. Lobban, R.G. Mallinson, Stud. Surf. Sci. Catal. 136 (2001) 43.
[24] B. Pietruszka, M. Heintze, in: A. Haljaste, T. Plank (Eds.), Proceedings of the HAKONE 8, Tatru, Estonia, 2002, p. 166.