Effects of Noble Metal Promoters on In Situ Reduced Low Loading Ni Catalysts for Methane Activation

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Abstract The commercial potential for a given catalytic process may be influenced by requirements on metal loading, in particular where noble metals are used. In an effort to substantially decrease the amount of catalyst material used for methane activation and catalytic partial oxidation (CPO), the effect of 0.005 wt% noble metal (Rh, Ru, Pd or Pt) on 0.5 wt% Ni/γ-Al$_2$O$_3$ catalysts have been studied at temperatures below 1,173 K and 1 atm. The successful catalysts were activated directly by in situ reduction, without a calcination step, to promote formation of a highly dispersed (supported) metal phase from nitrate precursors. The obtained metal particles were not observable by XRD (size < 2–3 nm). This activation procedure had a decisive effect on catalyst activity, as compared to a catalyst which was calcined ex situ before in situ reduction. Adding a noble metal caused a significant drop in the ignition temperature during temperature programmed catalytic partial oxidation (TPCPO). The ignition temperature for partial oxidation coincides well with the temperature for methane dissociation, and is likely correlated to the reducibility of the noble metal oxide. Methane partial oxidation over 0.5 wt% Ni catalysts, both with and without promoter, yielded high selectivity to synthesis gas (>93%) and stable performance for continued operation, but synthesis gas production at temperatures below 1,073 K required a promoter when the catalyst was ignited by TPCPO. Ignition of the CPO reactions by introducing the feed at a high furnace temperature (1,073 K) also enabled formation of synthesis gas, but the reaction was then less stable than obtained with the TPCPO procedure. A dual bed concept attempted to beneficially use the activation and combustion properties of the noble metal followed by the reforming properties of Ni. However, it was concluded that co-impregnated catalysts yielded as high, or even higher conversion of methane and selectivity to synthesis gas.

1 Introduction

Catalytic partial oxidation (CPO) of light hydrocarbons is one of several possible methods for producing hydrogen or synthesis gas [1]. It was suggested already in 1929, but the success of steam reforming [2, 3], and the poor yields of synthesis gas reported by Prettre et al. [4] left CPO rather unexplored until the early 1990s [5–7]. Today this process for the conversion of natural gas to synthesis gas is a maturing field of research, as evidenced by several review papers [8–11].

The activation of methane is typically studied either at a fixed furnace temperature or by employing temperature programmed methods. Ferreira-Aparicio et al. [12] studied the activation of methane over reduced transition metals supported on Al$_2$O$_3$ and SiO$_2$. The procedure involved heating at 10 K/min, where the catalyst was placed inside a continuous flow apparatus and exposed to 7 vol% CH$_4$ in helium at 150 kPa. The dissociation of methane was found to initiate at about 575 K for 5 wt% Ni on Al$_2$O$_3$. CO evolution, however, initiated at a lower temperature of

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about 525 K. This formation of CO requires the presence of oxygen species (NiO, OH), potentially remaining from the calcination at 773 K (3 h), or resulting from impurities of O_2 in the feed. Another study showed that the temperature for methane activation over calcined (1,200 K, 4 h) NiO depends strongly on the support when supported on alkaline earth oxides [13]. In this case activation of methane was not observable at temperatures below 873 K.

Catalysts prepared from nitrate precursors are typically calcined in order to remove residual NO^{2-}_3 and transform metal cations into metal oxide particles. In situ reduction is another method by which the metal cations can be reduced directly to metal particles [14]. At low temperatures the latter technique has proven to yield more highly dispersed metal particles [15], while calcination followed by reduction typically yields particles that are more strongly bound to the support oxide.

Ni is known to form spinel structures with alumina [16–19]. These structures are difficult to reduce, and at very low loadings, the impregnated Ni may form a two-dimensional surface spinel instead of merging into metal or metal oxide particles. To avoid deactivation from bulk spinel formation, a high loading of Ni is typically used when supported on alumina. Increased support interactions may also occur on supports other than alumina. It has been reported that the NiO phase formed during CPO over 8 wt% Ni/TiO_2 was more difficult to reduce by temperature programmed reduction as compared to a freshly calcined sample (973 K) [20].

From a mechanistic point of view the activation of methane on a reduced surface appears to be the rate limiting step in steam methane reforming, CO_2 reforming and methane dissociation [21]. Whether this is so during CPO is not entirely clear yet. Since transport limitations typically are present during CPO at higher temperatures [22] it is difficult to address the catalytic potential of the metal or metal oxide at relevant conditions. Reaction mechanisms over transition metal catalysts were recently reviewed [11]. Although inherent differences exist over transition metals depending on support interactions and promoters, effects of local concentrations of reactants and products changing rapidly throughout the bed may be just as important for the overall observable reaction mechanism.

It was recently shown by us [23] that supported 0.5 wt% Ni catalysts yielded high selectivity to synthesis gas (>95%) and stable performance for 5–10 h operation, but only when the catalysts were reduced in situ. Calcining low loading (0.5 wt%) Ni catalysts was reported to be detrimental to their activity and selectivity in catalytic partial oxidation of methane, most likely due to strong metal support interactions. The conclusion was supported by results from temperature programmed dissociation of methane, where activation occured at lower temperatures for the catalysts reduced directly in situ as compared to the
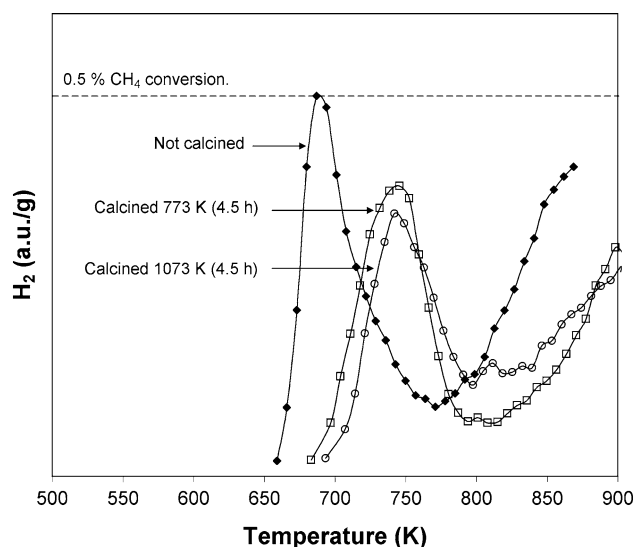

Fig. 1 TPDM over 200 mg 0.5 wt% Ni/10.3wt% Ce/α-Al_2O_3, heating from ambient to 1,073 K at 5 K/min in 156 Nl/g h 3.8% CH_4 in N_2. Prior to methane dissociation the catalysts were reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2. Almost identical results were obtained on 0.5 wt% Ni/α-Al_2O_3. 10.3wt% Ce/α-Al_2O_3 did not contribute to methane activation [23]

catalysts calcined prior to reduction, as shown in Fig. 1. Calcination was also reported to increase recombination chemistry to ethene and ethane on 0.5 wt% Ni catalysts. Increased duration of high temperature reduction (1,073 K) was shown to have a negative effect on both the activation temperature and the total amount of methane which dissociated over 0.5 wt% Ni/γ-Al_2O_3, Fig. 2. It was suggested
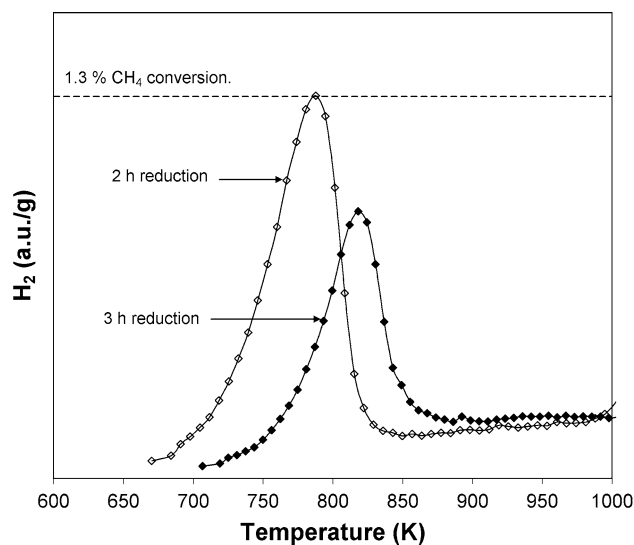

Fig. 2 TPDM over 200 mg 0.5 wt% Ni/γ-Al_2O_3, heating from ambient to 1,073 K at 5 K/min in 81 Nl/g h 7.4% CH_4 in N_2. The impregnated catalyst precursors had been reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2 [23]

that this could be related to the growth of Ni(111) surfaces at the expence of Ni(110) or Ni(100), since it is known that the latter show a higher probability for methane dissociation [24].

Beneficial effects of noble metal addition to Ni catalysts have been reported in the literature. Choudhary et al. [25] studied ignition temperatures over high loading Ni (18.7 wt%) catalysts promoted by noble metals (0.1, 0.5 or 2.5 wt%) including Ru, Pd and Pt. Nakagawa et al. [26] studied mixed bimetallic catalysts of Ni and Ir supported on La_2O_3, which were calcined at 873 K for 5 h before catalytic testing. At a furnace temperature of 873 K the bimetallic catalyst with 0.25 wt% Ir and 0.5 wt% Ni was less susceptible to carbon deposition and produced comparable amounts of synthesis gas as compared to bimetallic catalysts with higher loadings of Ni. Other supports were also tested and the catalyst performance depended strongly on the chosen support, with La_2O_3 and Y_2O_3 yielding the best results.

Basile et al. [27, 28] reported beneficial effects of Rh addition to a Ni catalyst, where the presence of Rh promoted the reduction of Ni, causing a higher amount of Ni to be present in a reduced state. Surface temperature profiles throughout the catalyst bed suggested differences in the distribution of heat, and thus possibly mechanistic differences related to the local concentration of reactant and product species for the Rh, Ni and the Rh–Ni catalysts. A similar promoter effect was reported for a Ni–Pt catalyst during oxidative steam reforming [29], where the resistance to hot-spot formation was higher for a sequentially impregnated catalyst, first Ni then Pt, as compared a co-impregnated catalyst. Sequential impregnation was also most beneficial for promoting the reducibility of Ni by Pt. Over Pt only linearly bonded CO was observed. Over the bimetallic catalysts both bridged and linearly adsorbed CO, as well as carbonyl species associated with Ni were observed.

Ji et al. [30] studied 8 wt% Ni/γ-Al_2O_3 promoted by 0.1 wt% Pt calcined at 873 K (4 h). Adding Pt caused a drop in the ignition temperature of about 100 K during temperature programmed surface reaction (10 K/min), and improved reducibility of Ni was reported from a TPR measurement. Dias and Assaf [31] studied a 15 wt% Ni/γ-Al_2O_3 catalyst promoted with <0.3 wt% Pd, Pt or Ir during autothermal reforming of methane. It was reported that at this high Ni loading the effect of adding a noble metal was to increase the metal surface area, effectively promoting the dispersion of Ni. An almost linear correlation between metal surface area and methane conversion was reported.

The price and availability of metal catalyst precursors, in particular with respect to the noble metals, may have a significant influence on the economy and commercial potential for a given catalytic process. It is therefore desirable, also from an environmental perspective, to minimize the use of catalyst materials. Our purpose was therefore to study low loading Ni catalysts (0.5 wt% Ni) and to promote these with extremely small amounts of noble metals. By modifying the Ni catalysts with 0.005 wt% Rh, Ru, Pd or Pt, we here illustrate the effects of such extremely low levels of noble metal modifiers on methane activation. This enables the start-up of low loading Ni catalysts from ambient temperatures following direct in situ reduction of impregnated catalyst precursors.

2 Experimental

2.1 Catalyst Preparation

All catalysts were prepared by incipient wetness (co)-impregnation of a high surface area γ-Al_2O_3 (156 m^2/g) using an aqueous solution of nitrate salt precursors, and subsequently dried in air at 383 K for 1 h. The catalysts are labelled by the metal weight fraction and the type of metal. For example the 0.5 wt% Ni + 0.005 wt% Ru/γ-Al_2O_3 has been given the label 0.5Ni0.005Ru.

2.2 Catalytic Partial Oxidation

Catalytic partial oxidation (CPO) of methane was carried out in co-feed modus in a quartz reactor (12 mm i.d.) at near-to atmospheric pressure. The tubular reactor contained an internal axial quartz tube (4 mm o.d.) equipped with a movable K-type thermocouple, thus enabling the measurement of gas temperatures.

The undiluted catalyst bed (1 or 2 mm, 100 or 200 mg catalyst) was located on top of a layer of inert α-Al_2O_3 (3 mm). A heat shield of α-Al_2O_3 (3 mm) was placed on top of the catalyst bed. The temperature and product composition were monitored as a function of the furnace temperature. The reactor set-up and equipment for GC analysis have been described in more detail elsewhere [32–35].

The furnace temperature and gas hourly space velocity were typically in the range 298–1,073 K and 60 Nl CH_4/g,h in air (CH_4/O_2 = 2), respectively, corresponding to a bed residence time of approximately 5–18 ms. The impregnated catalysts were reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held at 1,073 K for a total of 2 h reduction in 200 Nml/min 15% H_2 in N_2. After 2 h reduction the reactor was isolated, and the catalyst was maintained in a reducing atmosphere while the CPO-feed was stabilized in a separate line for about 1 h. The stabilized feed was then switched to the reactor.

Temperature programmed catalytic partial oxidation (TPCPO) was used to investigate the effect of noble metal

addition on the ignition temperatures. The catalysts were reduced as described above and cooled down to ambient before heating at 10 K/min up to 1,073 K in 60 Nl CH_4/g h in air ($CH_4/O_2 = 2$).

A dual bed (DB) concept was used for investigating possible effects related to the co-impregnation and co-location of Ni and noble metal. A layer of Ni catalyst (1 mm) was placed on top of a layer of inert α-Al_2O_3 (3 mm), and covered by a layer of noble metal catalyst (1 mm). A heat shield of α-Al_2O_3 (3 mm) was placed on top of the dual catalyst bed. Temperature programmed CPO (DB-TPCPO) was carried out in the same way as for TPCPO, with the same amount of feed.

2.3 Catalyst Characterization

Temperature programmed reduction (TPR) was used to investigate the direct reduction of the impregnated catalyst. The reactor set-up was the same as used for CPO. The reduction was carried out by heating at 10 K/min in 78 Nl/g h 3.7% H_2 in N_2. The reduction was monitored using a mass spectrometer (GASLAB 300).

Methane activation was investigated by temperature programmed dissociation of methane (TPDM). The reactor set-up was the same as used for CPO, and the catalyst pretreatment was also identical. After reduction the catalyst was cooled to ambient in 300 Nml N_2/min before the temperature program was started. Heating at 5 K/min up to 1,073 K in 7.4% CH_4 in N_2 at 6 Nl CH_4/g h, the H_2 evolution was monitored using a mass spectrometer (GASLAB 300). For the most relevant temperature range to CPO in this study, methane activation from dissociation was found to be insignificant over the support material, as illustrated in Fig. 3.

X-ray diffraction spectra were obtained using a Bruker-AXS D8 Focus X-ray diffractometer with monochromatic CuK_α radiation. The catalysts were pretreated in a similar way as before CPO, and the results were used to verify the presence of a highly distributed Ni phase. After exposure to air at ambient temperatures neither NiO nor metallic Ni could be observed by XRD, indicating a Scherrer thickness, and also potentially particle sizes below 2–3 nm.

3 Results and Discussion

3.1 Reduction of Precursors and CH_4 Activation over 0.5Ni

The direct reduction of the impregnated 0.5 wt% Ni catalyst precursor was studied using temperature programmed reduction (TPR). Figure 4 illustrates that the reduction of the nitrate precursors during TPR (10 K/min, 3.7% H_2)
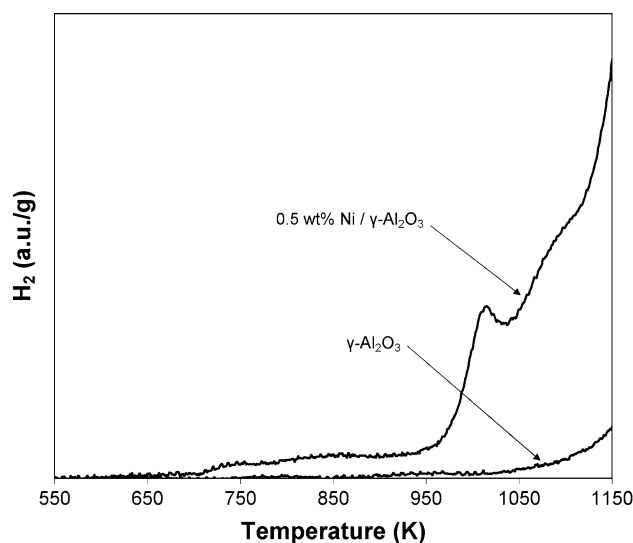
Fig. 3 TPDM over support material (γ-Al_2O_3) as compared to a Ni catalyst (0.5 wt% Ni/γ-Al_2O_3). Activation was initiated by heating from ambient to 1,173 K at 10 K/min in 81 Nl/g h 7.4% CH_4 in N_2. The impregnated catalyst precursors (200 mg) had been reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2
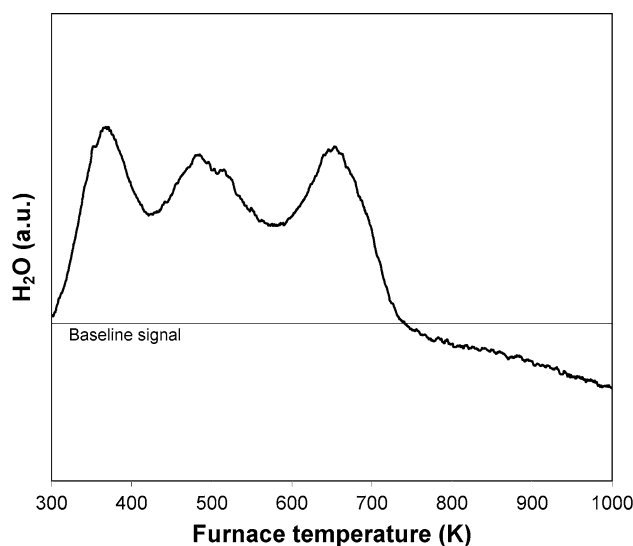

Fig. 4 TPR of 100 mg freshly impregnated catalyst (0.5Ni), heating from ambient to 1,073 K furnace temperature at 10 K/min in 78 Nl/g h 3.7% H_2 in N_2

proceeds readily in the temperature interval below 800 K. This indicates that the reduction temperature for in situ reduction before CPO (1,073 K) is sufficient for obtaining a reduced catalyst.

Temperature programmed dissociation of methane and temperature programmed catalytic partial oxidation (TPCPO) of methane were studied over in situ reduced 0.5 wt% Ni catalysts (0.5Ni). Figure 5 compares the activation temperatures for these two processes as a function of

methane conversion in the case of TPCPO, and hydrogen formation in the case of TPDM. It illustrates that over reduced catalysts the activation of methane initiates above 600 K, but is rather slow until the temperature reaches 950–1,000 K.

From Fig. 5 it may be concluded that the oxidative conversion of methane obtained during TPCPO and the activation of methane during temperature programmed dissociation coincides when plotted versus the temperature. This may suggest that the dissociation of methane is the common rate limiting step for methane conversion during start-up of CPO, as it has previously been shown to be during steady-state for steam reforming and dry reforming [21].

In Fig. 6 the product formation obtained during TPCPO is illustrated as a function of furnace temperature. Because compressed air was used as oxidant the initial concentration of CO_2 is not zero. Following the direct in situ reduction prior to TPCPO, it is expected that the catalyst may be oxidized by the feed during TPCPO in the temperature range from ambient to about 600 K. Once the temperature reaches 600 K there is an increase in the flow of CO_2, indicating that combustion is taking place, most likely involving lattice oxygen.

Above 700 K the interaction of methane with the catalyst appears to have created reduced sites leading to the formation of H_2 and CO, Fig. 6, as reduced sites are generally required for H_2 formation during CPO. In general, it may be expected that as the temperature is increased more
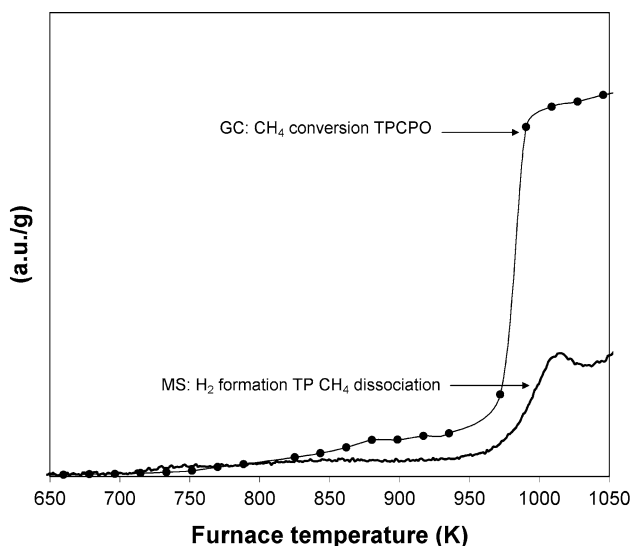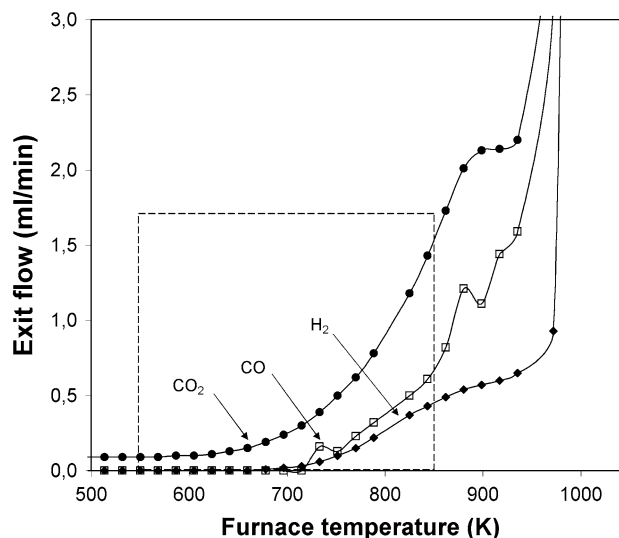

Fig. 6 Illustrating the evolution of CO_2 prior to CO and H_2 during TPCPO of methane over 0.5Ni, heating from ambient to 1,073 K furnace temperature at 5 K/min and 60 Nl CH_4/g h. The catalyst precursors (200 mg) had been reduced in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2

sites are reduced by the interaction of methane and H_2 with lattice oxygen. However, at first the reactions proceed slowly, and the presence of gas phase oxygen is likely to cause re-oxidation of some of the reduced sites. Once the temperature reaches 960–980 K there is a light-off, and as already mentioned, this ignition coincides with a rapid increase in hydrogen formation during temperature programmed dissociation of methane.

If oxygen-assisted activation of methane occurs, then this reaction pathway does not include a rate limiting step with a significantly lower activation energy barrier, as compared to the mechanism involving pyrolysis followed by oxidation. However, even if assuming that the dissociation of CH_3 to CH_2 and H is the rate limiting step for ignition in CPO, the reaction mechanism may still involve an oxidative route to CO through CH_2O and/or CHO. The results in Fig. 5 do not contradict this possibility, and here we do not speak about the mechanism at steady-state. At steady-state the conditions on the catalyst surface and through the catalyst bed are likely to be significantly different from those present before and during ignition.

3.2 Noble Metal Effects on Ignition and Selectivity

Temperature programmed catalytic partial oxidation was carried out over a series of catalysts. The purpose was to discern potential effects from adding 0.005 wt% of Rh, Ru, Pd or Pt to 0.5 wt% Ni/γ-Al_2O_3.

Figure 7a–d illustrates that noble metals ignite the CPO reactions at significantly lower temperatures as compared

Fig. 5 Illustrating the coincidence of methane activation during TPDM and TPCPO over 0.5Ni. The catalyst precursors (200 mg) were reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2. After cooling to ambient, the reaction was carried out subsequently by heating to 1,073 K furnace temperature at 10 K/min in 81 Nl/g h 7.4% CH_4 in N_2 or 60 Nl CH_4/g h in air (CH_4/O_2 = 2)
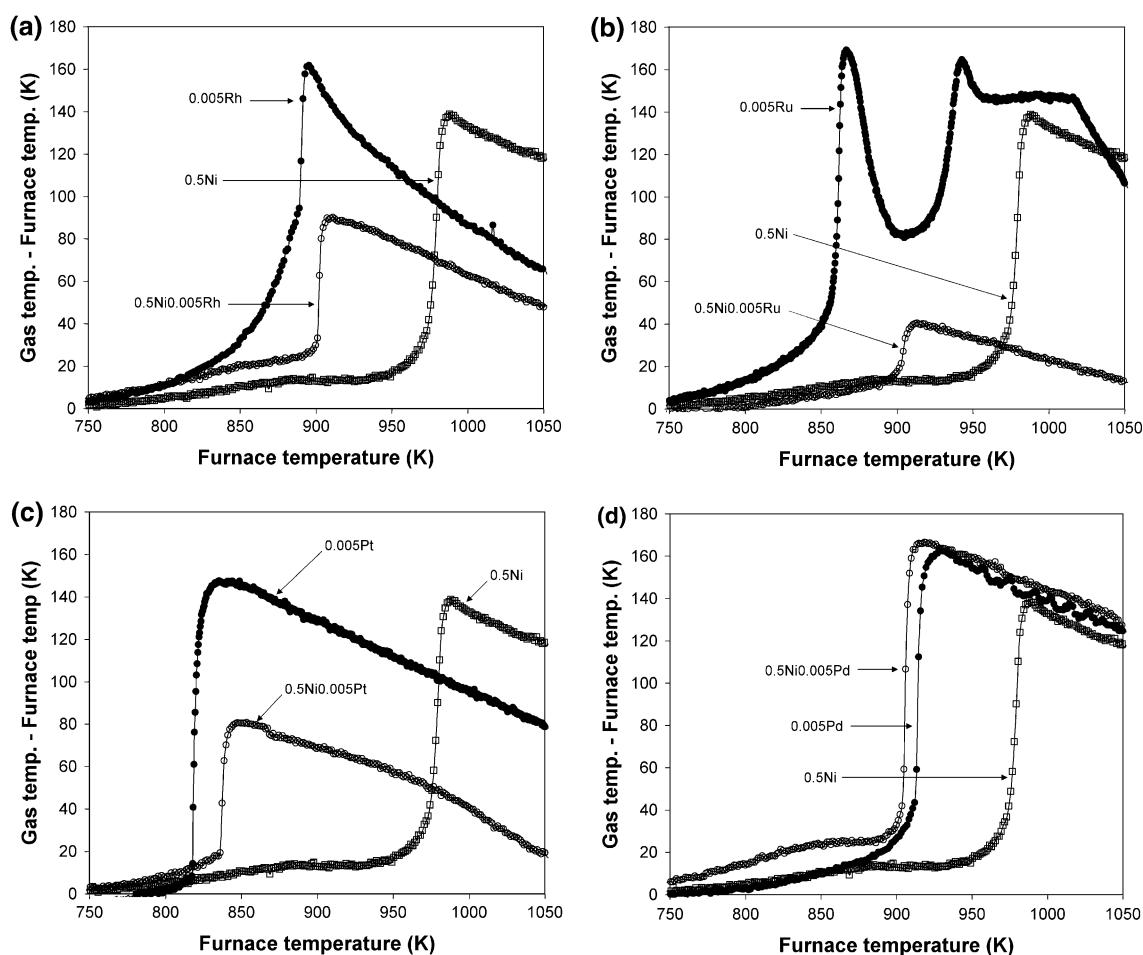
Fig. 7 TPCPO of methane over different catalysts obtained by heating from ambient to 1,073 K furnace temperature at 5 K/min and 60 Nl CH_4/g h. The impregnated catalyst precursors (200 mg) had been reduced directly in situ by heating at 10 K/min from ambient to 1,073 K, and held 2 h at 1,073 K in 200 Nml/min 15% H_2 in N_2.

Illustrating the effect of noble metal modifiers on the ignition furnace temperature for 0.5 wt% Ni catalyts, as well as ignition furnace temperatures for 0.005 wt% noble metal catalysts **a** Rh, **b** Ru, **c** Pt and **d** Pd, all supported on γ-Al_2O_3 (156 m^2/g)

to Ni, and the presence of a noble metal has a significant effect on the ignition temperature of modified Ni catalysts. This was expected since noble metals are known to promote the reduction of Ni. In general, such promotion is likely related to a combination of spillover [36, 37] and electronic effects. For example, the presence of Pt has been shown to promote the reduction of a Ni catalyst during temperature programmed reduction [36].

An intimate contact between the noble metal and non-noble metal is to some degree required, but co-impregnation is not necessary [37]. The presence of water prior to, or the formation of water during TPR, is known to increase transport of spilt-over hydrogen ions, thus enabling the reduction of the non-noble metal at lower temperatures [36, 37].

The formation of hydrogen and CO, as well as the conversion of methane during TPCPO, are all illustrated in Fig. 8a–f. The formation of synthesis gas was promoted

during ignition by adding 0.005 wt% of the noble metals Rh, Ru and Pt to a 0.5 wt% Ni catalyst. The effect of adding Pd was not significant with respect to improving the formation of H_2 or CO during ignition. Of important relevance to the mechanism of ignition, it is observed that for some of the catalysts the formation of H_2(g), although insignificant in amount, appears to initiate prior to the formation of CO(g), Fig. 8c–f. This appears to be true for all catalysts, perhaps except for the 0.005 wt% Pt catalyst. The very low barriers to OH formation over Pt, which have been reported in mechanistic studies [38, 39], may be the reason for this difference.

Not illustrated in Fig. 8a–f is the formation of products due to coupling reactions, such as those leading to ethene and ethane. Coupled products were observed over 0.5Ni, as well as for 0.005Ru, 0.005Pd and 0.5Ni0.005Pd. The selectivity to ethene was typically <2%, and for ethane it was <1%. The conditions investigated did not contribute to
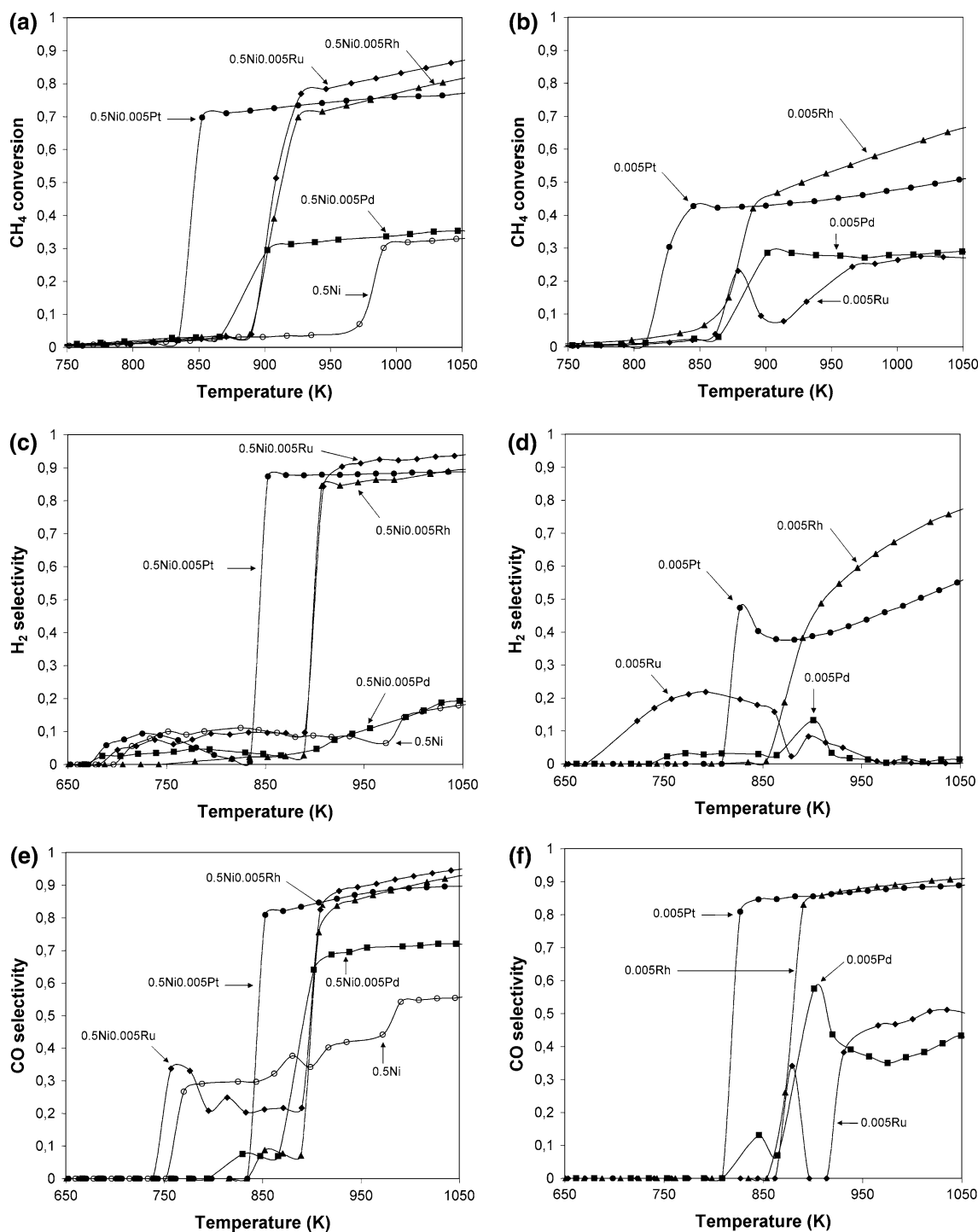
Fig. 8 Illustrating further details from TPCPO of methane, as described in Fig. 7. Showing conversion of methane (**a**, **b**), selectivity to hydrogen (**c**, **d**), and selectivity to CO (**e**, **f**) as functions of measured gas temperature (K)

detectable formation of coupled products over the other catalysts.

The ignition profile of 0.005 wt% Ru catalyst is particularly interesting as it shows two distinct peaks, Fig. 7b. The drop in gas temperature in between the two ignition peaks coincides with a drop in methane conversion, H$_2$

selectivity and CO selectivity, Fig. 8b, d and f. It is suggested that this behaviour is related to the oxidation state of Ru, which may be interpreted to transition from one oxidation state before ignition and through an intermediate oxidation state where the conversion is temporarily decreased. Further studies with in situ X-ray absorption

spectroscopy may shed valuable light on the working states of these catalysts, but this was not within the scope of this project.

In this study the catalysts were co-impregnated and reduced directly in-situ. Although not investigated experimentally, there is a potential for the formation of bimetallic species or mixed oxides. In general, it is expected that the interaction of two different metals causes perturbations in their electronic structure [40], which again affects the binding energies of reactant and product intermediates, and thus also the elementary reaction barriers.

The reduction and removal of an oxygen atom from a metal oxide ($M_x^{\delta+}O_y^{\delta-}$) involves a charge transfer from the oxygen atom to the neighbouring metal atom(s). We have already mentioned that spillover effects, as well as electronic effects, may be involved in how noble metals promote the reduction of non-noble metals. In a bimetallic mixed oxide the M_1–O–M_2 bond strengths will depend on the inherent electronic structure of the metals. In general, the reduction of a mixed oxide will proceed in the direction that most rapidly minimizes the free energy.

Although the properties of a catalyst surface differs from that of the bulk, we here assume that the ignition over a metal oxide catalyst is somehow related to the change in free energy obtained by removing the oxygen atoms one by one. Therefore, incorporating a metal oxide with a higher ΔG per oxygen atom will decrease the ignition temperature, if these metals are reducible at the relevant conditions. This is what we observed in the presented study. A linear relationship between the ignition temperature and M–O bond strength has previously been reported for reactions of ethane and air over Pt, Pd, Rh and Ir foils [41].

Figure 9 illustrates the furnace temperatures at ignition as functions of the average change in free energy ΔG from the reduction of lattice oxygen at the ignition furnace temperature. These changes in free energy were calculated using the HSC CHEMISTRY 5.1 software package. RuO_2 has been included with the assumption that it is related to the second ignition peak over the Ru catalyst. The almost linear correlation between the thermodynamic values (ΔG) and the ignition furnace temperatures during TPCPO are possibly somewhat coincidental. This is when considering that the catalyst temperature is not known and only the furnace temperature is used for correlations. Using a lower heating rate than 10 K/min may improve the accuracy of the ignition temperatures if absolute correlations to thermodynamics are sought. Nevertheless, there appears to be a general trend.

3.3 Steady-State CPO

Methane conversions and synthesis gas selectivities obtained during CPO are here compared for all the
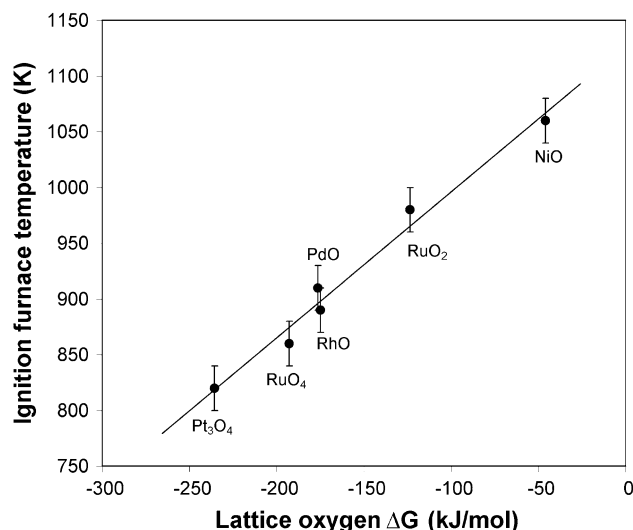

Fig. 9 The ignition furnace temperature ±20 K plotted versus the average change in Gibbs free energy ΔG associated with the reduction of a lattice oxygen. Free energy changes were calculated at the ignition furnace temperature using the HSC CHEMISTRY 5.1 software package. The *vertical lines* indicate that there is uncertainty associated with the actual ignition temperatures

different catalysts at steady-state 1,073 K furnace temperature and 1 atm. These comparisons are based on three different approaches to steady-state operation, including ignition at the steady-state furnace temperature (SSCPO), TPCPO followed by steady-state CPO (TPCPO–SSCPO) and a dual bed (DB) concept (DB-TPCPO-SSCPO). The results from these tests are summarized in Tables 1 and 2.

The two runs with 0.5Ni (SSCPO) illustrate that the catalyst performance is very sensitive to this start-up procedure. Figure 10 compares CH_4 conversion during the first couple of hours in the two runs with 0.5Ni. In the second run there was an initial 2 h period with a substantial linear deactivation. The state of the catalyst surface during this period, including its carbon depository, is unknown. However, the observation of C_{2+} in the product stream, first appearing after this initial period of deactivation, is potentially induced by the period of deactivation.

We suggest that the start-up sensitivity is related to carbon deposition effectively blocking more and more active sites with time on stream until a steady-state between methane dissociation and oxidation is reached after some hours. We have recently illustrated how C_{2+} formation is influenced by incomplete oxygen conversion [33], and argued that this is likely related to localized conditions, either on the catalyst surface due to a surplus of CH_x intermediates, or involving hetero-homogeneous coupling, both potentially enabling the formation of higher hydrocarbons.

An initial tendency to deactivation during the first 1–2 h of operation, was observed for almost all catalysts (SSCPO,

Table 1 Steady-state CPO of methane after 8–60 h TOS, 60 Nl CH$_4$/g h (100 mg catalyst) at 1,073 K furnace temperature and 1 atm

SSCPO[a]	TOS (h)	X:CH$_4$ (%)	S:H$_2$ (%)	S:CO (%)	S:C$_{2=}$ (%)	S:C$_{2-}$ (%)	Comments
Equil. (1,073 K)	–	94.7	98.1	98.0	–	–	–
0.5Ni	10	89.6	94.6	94.6	–	–	Stable
0.5Ni	20	79.3	88.9	92.3	0.4	0.1	Stable
0.5Ni0.005Rh	20	75.0	87.6	87.0	–	–	Stable
0.5Ni0.005Ru	40	88.3	93.0	93.8	–	–	Stable
0.5Ni0.005Pd	40	85.0	90.0	94.1	–	–	Stable
0.5Ni0.005Pt	60	88.4	93.3	93.6	–	–	20+ h activation
0.005Rh	20	68.0	79.0	91.8	–	–	Slow deactivation
0.005Ru	20	68.4	81.9	86.3	–	0.2	Unstable
0.005Pd	20	18.0	1.0	30.0	2.5	1.4	Slow deactivation
0.005Pt	20	43.0	42.0	78.2	–	–	20+ h activation

[a] Steady-state CPO initiated at 1,073 K furnace temperature. X conversion, S selectivity, C$_{2=}$ ethene, C$_{2-}$ ethane

Table 2 Steady-state catalytic partial oxidation of methane after 8-60 h TOS, 60 Nl CH$_4$/g h (100 mg catalyst) at 1,073 K furnace temperature and 1 atm

	TOS (h)	X:CH$_4$ (%)	S:H$_2$ (%)	S:CO (%)	S:C$_{2=}$(%)	S:C$_{2-}$ (%)	Comments
TPCPO–SSCPO[a]							
0.5Ni	8	29.8	7.8	55.6	3.0	1.0	Slow deactivation
0.5Ni0.005Rh	20	84.5	90.4	93.6	–	–	Stable
0.5Ni0.005Ru	20	89.5	95.1	95.4	–	–	Stable
0.5Ni0.005Pd	20	31.4	7.6	61.9	1.0	1.0	Slow deactivation
0.5Ni0.005Pt	20	88.0	93.8	94.2	–	–	Stable
0.005Rh	20	71.3	81.3	91.8	–	–	Stable
0.005Ru	20	33.8	11.0	70.5	1.0	1.0	Unstable
0.005Pd	20	17.4	0.5	19.4	2.0	0.6	Slow deactivation
0.005Pt	20	48.9	49.5	91.2	–	–	Slow deactivation
DB-TPCPO-SSCPO[b]							
0.005Rh‖0.5Ni	20	85.5	92.9	91.8	–	–	Stable
0.005Ru‖0.5Ni	20	72.0	85.0	87.6	–	0.2	Slow deactivation
0.005Pd‖0.5Ni	20	36.4	26.8	60.4	2.0	0.8	Stable
0.005Pt‖0.5Ni	20	69.6	81.8	84.4	–	–	Slow deactivation

[a] Steady-state CPO after temperature programmed CPO from ambient to 1,073 K furnace temperature at 5 K/min

[b] Dual bed, steady-state CPO after temperature programmed CPO from ambient to 1,073 K furnace temperature at 5 K/min

not illustrated), although not as severe as illustrated for 0.5Ni in Fig. 10. However, there were two exceptions, both involving Pt (0.005Pt and 0.5Ni0.005Pt). As illustrated in Fig. 11, after ignition at 1,073 K there was a long period of deactivation, potentially involving a significant restructuring of the surface. After 18–20 h on stream, there was an abrupt increase in methane conversion, and the catalysts transitioned to a different steady-state mode of operation. The comparison of 0.5Ni0.005Pt and 0.005Pt illustrates that this effect is related to Pt and its interaction with Ni, and not inherently due to the Ni.

The 0.5Ni0.005Pt catalyst operated for 68 h with no apparent deactivation once the catalyst had been conditioned for about 20 h. It reached a very high level of methane conversion and synthesis gas selectivity, as given in Tables 1, 2. This is probably the catalyst with the best potential for further studies on applications of modified low loading Ni catalysts. From a commercial point of view, the application of direct in situ reduction may cut costs related to catalyst production by a substantial factor. It may even be suggested that such catalysts can be rejuvenated and re-impregnated in situ if deactivated. In situ re-activation is commercially desirable because it decreases valuable down-time, and may cut costs related to catalyst unloading and reloading, not to mention the cost of new catalyst and support material.

The Ru catalysts were found to be inherently unstable, as illustrated in Fig. 12a, b. A possible relationship
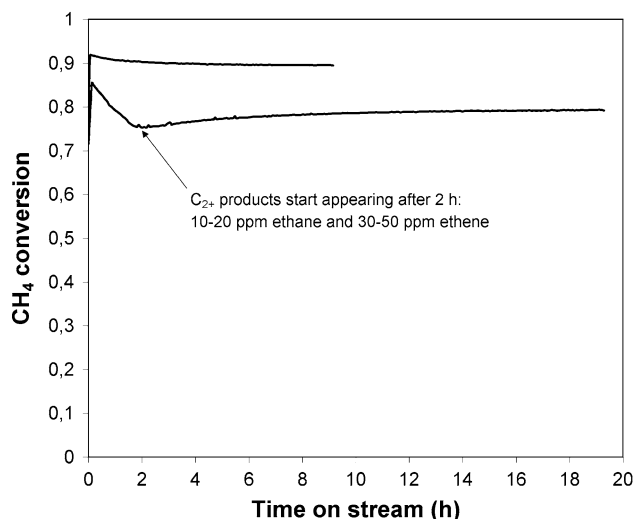
Fig. 10 SSCPO of methane over 0.5Ni, 60 Nl CH$_4$/g h (100 mg catalyst) at 1,073 K furnace temperature and 1 atm. Illustrating methane conversion as a function of time on stream for the two runs in Tables 1, 2 (SSCPO)
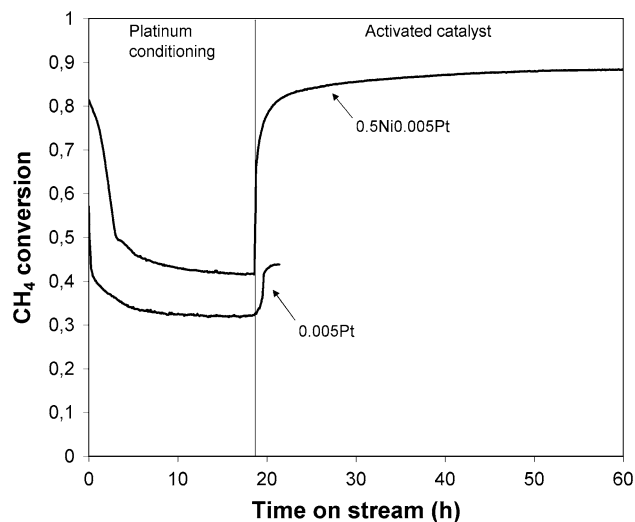

Fig. 11 SSCPO of methane over 0.5Ni0.005Pt and 0.005Pt, 60 Nl CH$_4$/g h (100 mg catalyst) at 1,073 K furnace temperature and 1 atm. Illustrating methane conversion as a function of time on stream for the two runs in Tables 1, 2 (SSCPO)

Fig. 12 CPO of methane over 0.005Ru, 60 Nl CH$_4$/g h (100 mg catalyst) at 1,073 K furnace temperature and 1 atm. Illustrating methane conversion and synthesis gas selectivity as functions of time on stream, comparing **a** ignition at 1,073 K furnace temperature (SSCPO), and **b** SSCPO at 1,073 K following TPCPO (TPCPO–SSCPO)

between this instability, the oxidation state and the crystal structure has already been suggested. The 0.005Ru catalyst was particularly unsuccessful with the TPCPO–SSCPO procedure, where the main products were CO and water. This tells us that the water-gas-shift reaction was far from equilibrated at these conditions.

The procedure involving ignition by TPCPO–SSCPO was generally more stable than start-up by switching the feed to the reactor at 1,073 K furnace temperature (SSCPO). However, for some of the catalysts the TPCPO–SSCPO method did not yield CH$_4$ conversion and synthesis
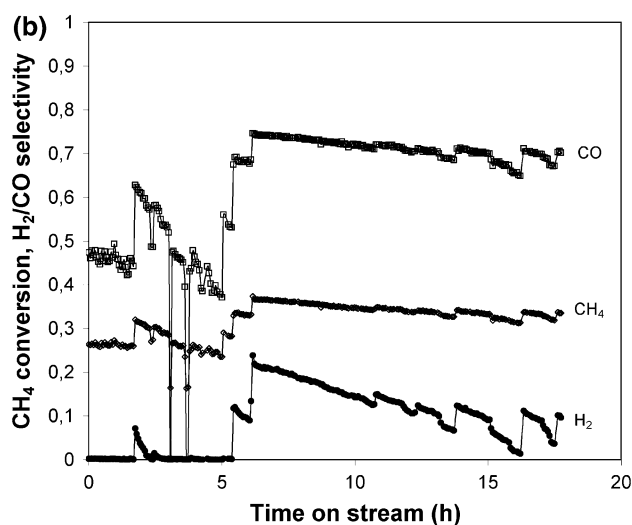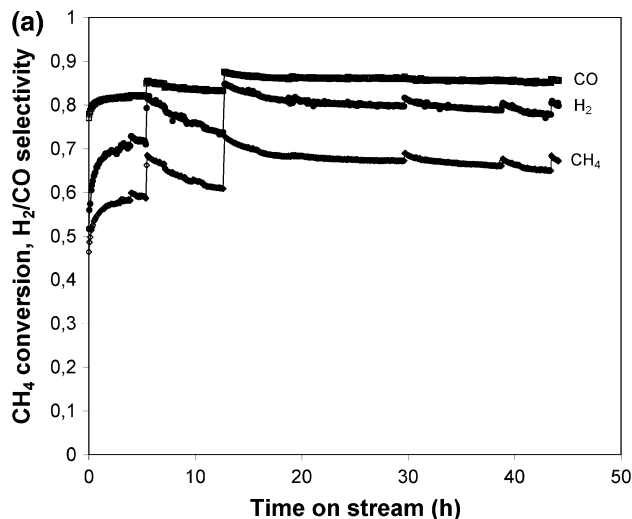
gas selectivity comparable to start-up at 1,073 K. In particular, for the 0.5Ni, 0.5Ni0.005Pd and 0.005Ru catalysts, ignition at 1,073 K furnace temperature was more suitable than TPCPO up to 1,073 K. In general, this is most likely related to the reducibility of the catalysts and how their oxidation state varies as a function of furnace temperature and gas phase composition. Co-feeding H$_2$ may be suggested as a remedy for maintaining a reduced catalyst during start-up.

The purpose of the dual bed testing was an attempt to beneficially use the activation and combustion properties of the noble metal followed by the reforming properties of Ni. However, both the Ru and Pt modified Ni catalysts performed better when the metals were co-impregnated. For

Pd the dual bed concept improved the selectivity to hydrogen, but this also caused an increase in the formation of C_{2+}. The Rh catalysts performed equally well as a dual bed concept and when co-impregnated.

4 Conclusions

Effects of adding 0.005 wt% Rh, Ru, Pd or Pt to 0.5 wt% Ni on alumina catalysts were investigated. Noble metal modifiers were shown to affect ignition profiles and the transition to steady-state catalytic partial oxidation of methane. The noble metal effect could be correlated to the reducibility of the noble metal oxide as compared to Ni oxide.

The activation procedure, involving direct in situ reduction of impregnated catalyst precursors had a decisive effect on activity and selectivity. Calcination of low loading Ni catalysts is not beneficial for synthesis gas formation.

The instability of Ru supported on alumina suggested the presence of structural-functional relationships, as the bulk structure of Ru is hexagonal closed packed, while the more stable catalysts, including Ni, Pt, Pd and Rh, all have bulk face centered cubic structures.

In general, the noble metal modifications of nickel catalysts enabled ignition at lower temperatures, as compared to the pure nickel catalyst, when the catalysts were heated from the ambient temperature (ca. 298 K) in a mixture of methane and air ($CH_4/O_2 = 2.0$). In particular, Pt and Rh were found to be highly beneficial. Pt required about 20 h of conditioning before transitioning to operational conditions where synthesis gas formation was promoted.

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