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Catalytic partial oxidation of methane over Ni-, Co- and Fe-based catalysts

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Abstract

Partial oxidation of methane to synthesis gas has been investigated over Fe-, Co- and Ni-based catalysts in fixed bed reactor in view of a possible application in a fluidized bed reactor. Catalytic testing of the oxidic catalysts show an increasing activity for total oxidation of methane in the following order: Fe_2O_3>CoO>NiO. After reduction of the metal, the Ni and Co catalysts give equilibrium conversion to synthesis gas. Co is much more easier oxidized compared to Ni at decreasing temperature under experimental conditions and equilibrium is not followed at temperatures below 550°C. Low reforming activity is obtained over the Fe catalyst. Investigations at 1000–1100°C are necessary to further explore Fe as a reforming catalyst.

Keywords: Methane conversion; Synthesis gas; Fe-, Co- and Ni-based catalysts

1. Introduction

It is generally assumed that the catalytic partial oxidation (CPO) of methane to synthesis gas may proceed according to two distinct routes, the direct and the indirect oxidation. For non noble metals like Ni, the most often suggested route is the indirect one, which consists of a primary total oxidation into H_2O and CO_2, followed by the reforming reactions into syngas [1–4].

The CPO process can be run in fixed bed or in fluidized bed reactors. The latter case provides a better temperature control, and it has been shown that less coking is observed, probably due to internal gasification of coke [5–7]. In addition equilibrium is easily obtained even with low contents of Ni [8]. At high temperatures (>600°C) the reforming equilibrium gives high yields of CO and H_2. At lower temperatures (300–400°C) the equilibrium gives low yields of synthesis gas and the reverse reaction, i.e., the syngas methanation may take place. Previous results indicate that this is the case in the reactor freeboard of the fluidized bed reactor. The reverse reaction probably proceeds on catalyst fines following the exit stream [8]. A possible solution to this could be the development of a catalyst that is active for the reforming reaction at high temperatures (>900°C) and inactive at lower temperatures (300–600°C).

It has been shown by several researchers that the reforming and the methanation reactions are catalysed by reduced metals (e.g. Ni) [9–11]. If the active metal is oxidised in the fluidized bed reactor at low temperatures (T<800°C), giving a catalyst that is not

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active for the methanation reaction, back-formation of methane could be avoided in the exit stream.

The purpose of this study is then to investigate in a fixed bed reactor the oxidation/reduction properties and the potential as a CPO catalyst of a series of Fe-, Co- and Ni-based catalysts, in view of an application in a fluidized bed reactor.

2. Experimental

Preparation of M/La/Al_2O_3, M=Ni, Co or Fe (1.7 wt.% La, approx. 5 wt.% M) were performed by modifying θ-Al_2O_3 (Condea, Scc-a5/90) with lanthanum nitrate (Alfa, ultrapure) using the incipient wetness technique. The carrier was calcined at 900°C for 12 h in air. After calcination the carrier had a surface area of 90 m^2/g. The carrier was then impregnated with $Ni(NO_3)_2{\cdot}6H_2O$ (KEBO Lab), $Co(NO_3)_2{\cdot}6H_2O$ (Janssen) or $Fe(NO_3)_3{\cdot}9H_2O$ (Merck) also by using the incipient wetness technique and thereafter calcined at 900°C for 12 h.

The reference catalyst Ni/Al_2O_3 was prepared by coprecipitating alumina with nickel hexamine solutions as detailed for cobalt in Courty et al. [12].

The materials were pressed into pellets, crushed and sieved to a particle size 0.2–0.3 mm (30–50 mesh) before use. Each catalyst (100 mg) was tested in a fixed bed quartz reactor (as explained in [4]) with inner diameter 0.4 cm. A thermocouple was placed at the outer reactor wall close to the catalyst bed. The feed was 100 ml/min (STP), with He:CH_4:O_2= 85:10:5. The diluted gases were used to avoid excessive heating. The catalyst was heated (20°C/min) in the reaction mixture to 500°C, and then stepwise (10°C/min, stable level of 5 min every 50 or 100°C) to the maximum temperature (900 or 950°C). The catalyst was then reduced in a stream of 5 vol.% H_2 in He at the maximum temperature before being cooled down to 500°C, according to the same procedure as during the heating step (unless otherwise specified).

The gas effluent was analysed on-line by gas chromatography (DELSI GC equipped with FID and TCD detectors and using Hayesep D and carbosieve SII columns, respectively). A quadrupole mass spectrometer (VG Pegasus) was also used to analyse the gas effluent. The GC analyses were used to calibrate the MS.

The amount of ferromagnetic Co and Ni was determined by magnetic measurements using the Weiss method in a special cell allowing both catalytic testing and magnetic measurements [13].

Temperature programmed reduction (TPR) experiments were performed on an Altamira instrument. A TC detector was used to analyse the effluent gas. The reductive gas was 10 vol% H_2 in Ar. The experiments were run in the temperature range of 50–1000°C with approximately 0.5 g sample, a temperature gradient of 20°C/min and a flow of 30 ml/min (NTP).

Elemental analysis were performed by inductively coupled plasma (ICP). Powder XRD experiments were run using Cu–$K_{\alpha 1+\alpha 2}$-radiation with a Philips PW1050/81 diffractometer equipped with a graphite monochromator.

3. Results

3.1. Thermodynamic calculations

The theoretical oxidation state of Ni, Co and Fe has been studied by thermodynamic calculations. At 1100°C and 17 bar total pressure theoretical calculations (Thermocalc [14]) gives an equilibrium pressure $P_{O_2}=3.75\times10^{-15}$ bar for a realistic CPO feed rate of $CH_4/O_2/H_2O/CO_2$=0.5/0.25/0.20/0.05 (which gives a H_2/CO ratio of 2 in the product stream). The calculated temperature over which the reduced metal is stable at this oxygen pressure is: Ni∼750°C, Co∼850°C, Fe∼1000°C.

These calculations indicate that the methanation activity at low temperature might be less for Co- and Fe-based catalyst due to reoxidation of the active metal.

3.2. Characterization

Characterization results for the catalysts are listed in Table 1.

Due to the low amount of metal (4 wt.%) supported on the La/Al_2O_3 catalysts, the main signal from XRD was θ-Al_2O_3. No indication of La containing compounds was observed with the three Ni-, Co- and Fe-based catalysts, as previously reported on similar Ni-based catalysts [9]. The formation of nickel aluminate $NiAl_2O_4$ (much likely) and $NiAl_{10}O_{16}$ (possibly) was

Table 1
Characterization data of the catalysts

Catalyst	Preparation method	Metal content (wt.%)	XRD (after calcination)	XRD (after testing)
Ni/1.7% La/Al_2O_3	Incipient wetness	4.3	θ-Al_2O_3, $NiAl_2O_4$, $NiAl_{10}O_{16}$[a]	Ni, θ-Al_2O_3, $NiAl_2O_4$, $NiAl_{10}O_{16}$[b]
Co/1.7% La/Al_2O_3	Incipient wetness	4.04	θ-Al_2O_3[c]	θ-Al_2O_3[d]
Fe/1.7% La/Al_2O_3	Incipient wetness	4.1	Fe_2O_3, θ-Al_2O_3, $FeAl_2O_4$[e]	θ-Al_2O_3, α-Al_2O_3, $FeAl_2O_4$
Ni/Al_2O_3	Coprecipitation	17.3	θ-Al_2O_3[f]	

[a] Shift in diffraction lines of θ-Al_2O_3 indicate the presence of $NiAl_{10}O_{16}$. Identification of $NiAl_2O_4$ is not possible due to overlapping with θ-Al_2O_3.
[b] Small shift in lines of θ-Al_2O_3 indicate that traces of $NiAl_{10}O_{16}$ might still be present.
[c] It is not possible to observe Co oxides (Co_2AlO_4/Co_3O_4/$CoAl_2O_4$) due to overlapping lines with θ-Al_2O_3.
[d] Metallic Co is not observed.
[e] Traces of $FeAl_2O_4$, lines partly overlapping with θ-Al_2O_3.
[f] Due to broad lines from θ-Al_2O_3 it is not possible to identify NiO or $NiAl_2O_4$.

observed on the Ni/La/Al_2O_3 catalyst. The formation of Fe_2O_3 and $FeAl_2O_4$ was observed on the Fe/La/Al_2O_3 catalyst. In contrast, it was not possible to identify metal oxides on the Co/La/Al_2O_3 or Ni/Al_2O_3 catalysts due to overlapping lines from θ-Al_2O_3 (see Table 1).

After the catalytic cycle during which the catalysts were exposed to hydrogen at the maximum temperature in order to obtain high yields to synthesis gas, metallic nickel was observed by XRD for the Ni/La/Al_2O_3 catalyst. In contrast, no metallic Fe or Co was detected for the Fe and Co containing catalysts. However, Fe_2O_3 was not observed after catalytic testing of the Fe containing catalyst, suggesting some reduction of the Fe(III) ions. For the case of the Co containing catalyst, it was still clear blue at the feed inlet (black at the outlet) indicating that Co oxides were present.

Fig. 1 reports the curves of temperature programmed reduction (TPR) of the catalysts. The degree of reduction calculated from the amount of consumed hydrogen as well as the reduction temperatures (peak maxima) are given in Table 2. The following features can be outlined:

Table 2
TPR reduction peaks and degree of reduction for the catalysts

Catalyst	Temperatures of peak maxima (°C)	Extent of reduction from H_2 consumption (%)
Ni/Al_2O_3	770	117[a]
Ni/La/Al_2O_3	400, 995	100[a]
Fe/La/Al_2O_3	320, 505, 790, 930	53[b]
Co/La/Al_2O_3	950	10[c]

[a] Assuming Ni(II).
[b] Assuming Fe(III).
[c] Assuming Co(II).

1. No consumption of hydrogen was observed during the TPR experiment carried out on the La/Al_2O_3 carrier.
2. A complete reduction of Ni/Al_2O_3 was obtained already at 771°C in accordance with the observations of Rynkowski et al. [15]. For the case of Ni/La/Al_2O_3 the complete reduction was observed at 997°C (assuming Ni(II)). This fits well with previous observed reduction temperatures for $NiAl_2O_4$ [15].
3. For the Fe/La/Al_2O_3 catalyst, 53% reduction was reached (assuming that Fe(III) reduces to metallic Fe) during the TPR experiment. The reduction of iron oxide proceeds in two stages, from Fe_2O_3 to FeO, then from FeO to Fe [16]. Assuming that all the Fe(III) ions were reduced to Fe(II) and that the next step led to metallic Fe, 53% reduction corresponds to 30% of the Fe existing as metal and the rest as Fe(II). According to Steinfeld et al. [16] pure Fe_2O_3 is completely reduced to metallic Fe in 2.3 vol.% H_2/Ar mixture after 25 min at 1000°C. $FeAl_2O_4$ is completely reduced to metallic Fe at 1010°C after 15 min [17]. Chen et al. [18] have shown that iron oxide supported on ZrO_2 after reduction exists in several oxidation states (Fe^{3+}, Fe^{2+}, Fe^0). After a TPR experiment of 4 wt.%

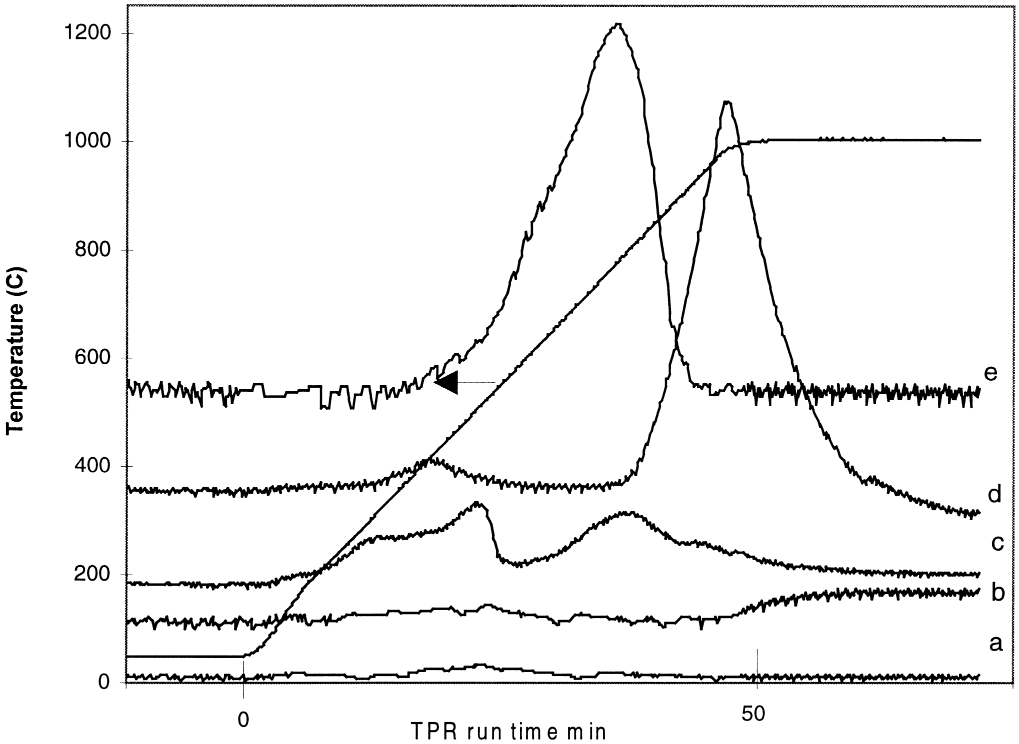

Fig. 1. TPR curves of (a) 1.7% La/Al_2O_3, (b) 5% Co/1.7% La/Al_2O_3, (c) 5% Fe/1.7% La/Al_2O_3, (d) 5% Ni/1.7% La/Al_2O_3, (e) 17% Ni/Al_2O_3. The data are normalised in order to represent the same amount of metal (in mole of Ni, Co or Fe) in each experiment.

Fe_2O_3/ZrO_2 at 700°C, the following distribution of iron was observed: Fe^0 58%, Fe^{2+} 26%, Fe^{3+} 16%. The reduction temperature was found to be dependent on the particle size of the iron oxide as well as the interaction with the carrier surface [18]. By comparing these literature data with the results obtained in this study, it can be deduced that a strong interaction between Fe and the carrier surface exists on the present catalyst giving less reducible solids.

4. Only 10% of the Co was reduced in the TPR experiment of Co/La/Al_2O_3, assuming Co(II) reduces to metallic Co. This fits well with the fact that stable Co oxides were reported to form on Al_2O_3 upon heating to high temperatures (>750°C) [19] as it is the case for our catalysts. Note, however, that the actual oxidation state of cobalt is more likely a mixture of Co(II) and Co(III) ions [20]. This means that the real extent of reduction to metal was even lower than 10%.

3.3. *Catalytic testing*

The catalysts were tested following a temperature cycle (increase and decrease) as described in the Section 2. The results for the series of tested catalysts are shown in Figs. 2–6.

As a general feature, mostly complete oxidation took place during the initial step of temperature increase in the reaction mixture. In contrast, high methane conversion and high selectivity to synthesis gas were generally observed after reduction at high temperature in hydrogen (or in the reacting feed) and at decreasing temperatures, except for the Fe-based material.

3.3.1. *Ni-based catalysts*

In the case of Ni/Al_2O_3 the total consumption of oxygen was first achieved at 750°C. High methane conversion and selectivity to CO were observed at 850°C upon heating in the reaction mixture (Fig. 2).

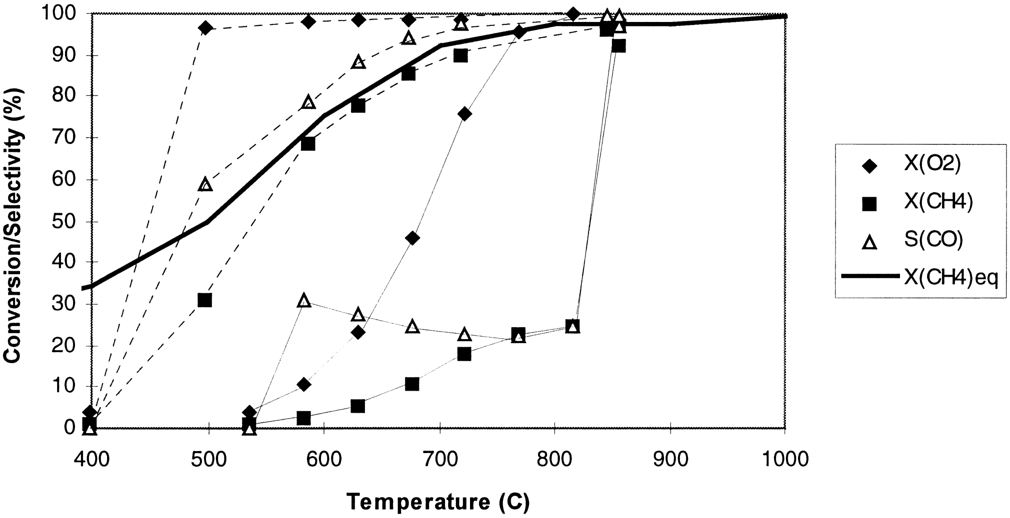

Fig. 2. Catalytic testing over Ni/Al_2O_3 at increasing and decreasing temperature. Increasing temperature: solid lines, decreasing temperature: dashed lines.

The thermodynamic equilibrium was obtained and maintained when decreasing the temperature down to about 600°C, in agreement with earlier works by Lunsford et al. [21] and by Swaan et al. [4]. In order to get more information about the initial change in selectivity, the activation of the catalyst was followed continuously by on-line mass spectrometry during the temperature programmed treatment in the reacting mixture, as illustrated in Fig. 3. In 6 s (heating rate of 10°C/min) the methane conversion increased from 20% to 95%. Simultaneously, the selectivities to CO and H_2 increased up to the values corresponding to the syngas formation equilibrium.

For $Ni/La/Al_2O_3$, the total O_2 consumption was observed at about 850°C but the reforming activity remained low even after heating in the reacting feed to 920°C. After reduction in H_2 for 1 h at 920°C, the catalyst was active for the reforming reaction (see Fig. 4) and equilibrium conversion to CO and H_2 was obtained.

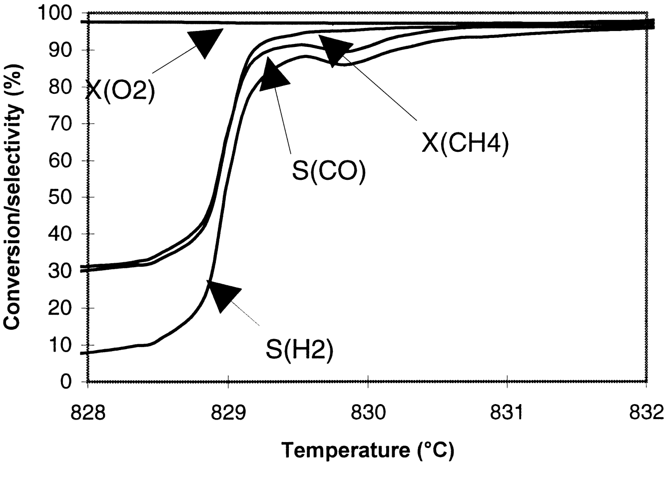

Fig. 3. The conversion and selectivity over Ni/Al_2O_3 at increasing temperature in feed.

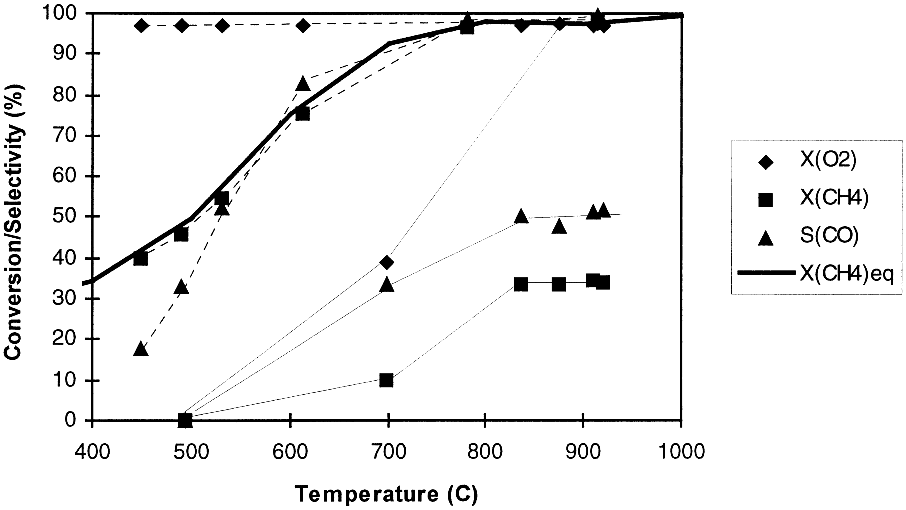

Fig. 4. Catalytic testing over $Ni/La/Al_2O_3$ at increasing and decreasing temperature. Increasing temperature: solid lines, decreasing temperature: dashed lines.

Magnetic measurements were performed on several Ni-based catalysts after the reduction in hydrogen at high temperature and at decreasing temperature under the reacting feed. The complete reduction (98–118%) of nickel, achieved after the reduction at high temperature was maintained under the reaction conditions even after catalytic testing for 105 min at 500°C. It has been proposed that NiC is the active surface species in CPO [11]. The precision/accuracy of the present magnetic measurements (about 20% relative uncertainty) seems to be somewhat unsatisfactory, and no conclusion as to the presence of a carbidic Ni phase can be drawn. After catalytic testing at 400°C for 105 min only 40% Ni was reduced and no conversion of methane was observed.

3.3.2. *Co-based catalyst*

In the case of $Co/La/Al_2O_3$ the total consumption of oxygen was obtained at about 750°C (see Fig. 5) and the catalyst was active mainly for the oxidation reaction even after heating in the reacting feed to 914°C. The catalyst was active for the reforming reaction after reduction in H_2, but at variance with the $Ni/La/Al_2O_3$ catalyst, the conversion decreased sharply at decreasing temperatures, far from the thermodynamic values: the conversion was almost suppressed already at 550°C. A similar observation was reported over co-precipitated M/La catalysts, M=Ni, Co [22], which would correspond to a much easier oxidation of Co compared to Ni.

Table 3
Magnetic measurements and catalytic test results of $Co/La/Al_2O_3$

Temperature (°C)	Treatment	Degree reduction (%)	D>150Å (%)	Oxygen conversion (%)	Methane conversion (%)	CO selectivity (%)
914	Reduced 1 h	1		94	34	39
960	Reduced 1 h	101	44	100	94	100
650	Cat test 105 min	101	49	96	65	76
550	Cat test 5 min	*		97	32	77
550	Cat test 35 min	*		73	18	0
550	Cat test 100 min	0		31	8	0
933	Reduced 1 h test 5 min	119	26	96	97	99

* – Magnetic measurements not performed.

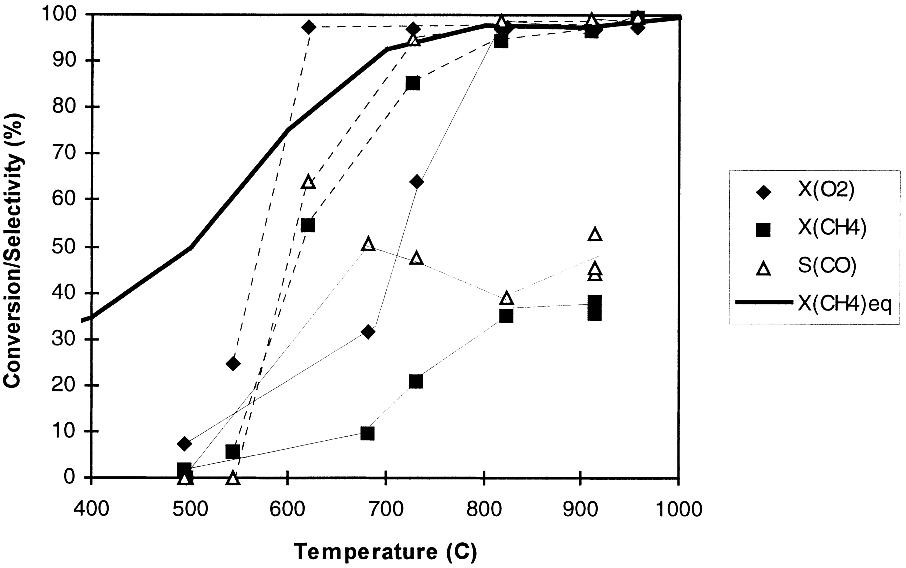

Fig. 5. Catalytic testing over Co/La/Al_2O_3 at increasing and decreasing temperature. Increasing temperature: solid lines, decreasing temperature: dashed lines.

The amount of reduced Co on Co/La/Al_2O_3 was followed by magnetic measurements at decreasing temperature in the feed mixture after reduction at 960°C in hydrogen. The results are given in Table 3. Initially, the Co phase was completely reduced, but with a poor dispersion since more than 40% of the particles had a diameter >150 Å [13]. By decreasing the temperature to 650°C, still only metallic Co was detected and somewhat lower conversion than equilibrium was achieved. At 550°C the Co was completely oxidised after 100 min in the reacting feed. In the mean time, the catalytic results showed a gradual decrease in methane conversion and CO selectivity (see Table 5). A new reduction of the catalyst in H_2 restored the metallic phase. A degree of Co reduction higher than 100% might be due to the accuracy of the magnetic measurement or a special magnetic effect for large metallic particles [13].

3.3.3. Fe-based catalyst

In the case of Fe/La/Al_2O_3, the total consumption of oxygen was observed already at 600°C but even after reduction in H_2 at 950°C for 1.5 h the methane conversion and the selectivity to CO remained low (Fig. 6). No significant difference in the curves was noted upon increasing or decreasing the temperature. This indicates that the catalyst was in the same state – non metallic – throughout the experiment, in agreement with thermodynamical estimates and the TPR experiments showing only a small formation of metallic Fe. In order to check if the catalyst could be reduced in a fuel rich mixture, the CH_4/O_2 ratio of the feed was increased. The results of these experiments are reported in Table 4: the CO selectivity increased only marginally upon increasing the CH_4/O_2 ratio.

In order to evaluate the reforming property of the Fe/La/Al_2O_3 catalyst, a separate run under CO_2 reforming conditions was performed: at 960°C after reduction in hydrogen, only 20% conversion of methane and carbon dioxide was obtained. This confirms the poor reforming ability of the Fe-based catalyst. However, it is not clear from our experiments

Table 4
Catalytic testing of Fe/La/Al_2O_3 at 960°C, each experiment was performed after reduction in 10% H_2 at reaction temperature

Feed CH_4:O_2:He	X (CH_4) (%)	S (CO) (%)
10:5:85	34	47
15:5:80	25	52
20:5:75	20	56

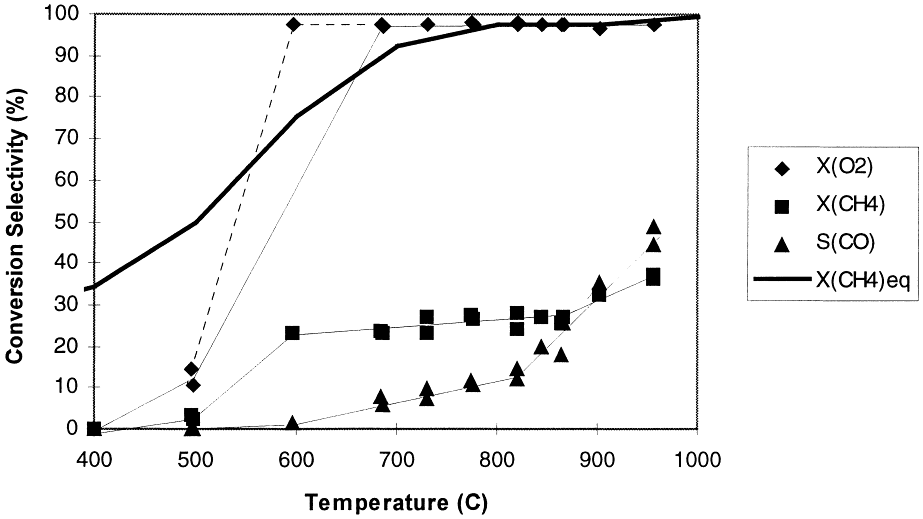

Fig. 6. Catalytic testing over $Fe/La/Al_2O_3$ at increasing and decreasing temperature. Increasing temperature: solid lines, decreasing temperature: dashed lines.

if we have Fe in reduced state under experimental conditions. Other studies indicate that Fe may present some reforming activity under highly reductive conditions, but at a much lower extent than for Ni [23,24].

4. Discussion

In order to evaluate the total oxidation properties of the tested catalysts, the lowest temperature at which oxygen was completely consumed and the corresponding CO selectivity are reported in Table 5. For all the catalysts the CO_2 yield is found to increase with temperature indicating oxidation properties.

It appears clearly that the Fe-based catalyst is much more active for total oxidation than the Co- and Ni-based solids. It may be noted also that a significant selectivity to CO is observed in the range of total oxidation while the selectivity to H_2 remains negligible for both the Ni (see both Table 6 giving the H_2/CO ratio and Fig. 4 giving the CO selectivity) and Fe-based catalysts (see both Table 6 giving the H_2/CO ratio and Fig. 6 giving the CO selectivity). This may be caused by further oxidation of partial oxidation products (catalytic or gas phase) with a higher rate

Table 5
Temperatures corresponding to the total consumption of oxygen and the related CO selectivities

Catalyst	Temperature for total oxidation (°C)	CO selectivity (%)
$Fe/La/Al_2O_3$	600	2
$Co/La/Al_2O_3$	750	45
$Ni/La/Al_2O_3$	750–850	35–45
Ni/Al_2O_3	750	25

Table 6
H_2/CO ratios obtained in the oxidation range (increasing temperature) and equilibrium values

Temperature (°C)	Equilibrium	Ni/Al_2O_3	$Ni/La/Al_2O_3$	$Co/La/Al_2O_3$	$Fe/La/Al_2O_3$
600	2.7	0	0	*	0
700	2.1	0.2	0	1.8	0
800	2.0	1.0	0	2	0
900	2.0	1.9	1.0	2	1.9

* – Not possible to estimate.

constant for the oxidation of H_2 compared to CO. Reforming/shift activity should according to equilibrium calculations give high H_2/CO selectivity at low temperatures. Influence of these reactions is, therefore, less likely.

It is also observed that the more stable Ni oxides on the La modified catalyst is less active for total oxidation than NiO on the Ni/Al_2O_3.

The Ni/Al_2O_3 catalyst was found to be reducible in the feed at temperatures higher than 830°C. The Ni/La/Al_2O_3 needs to be treated in H_2 at high temperature to be fully reduced, as required for reforming performance. A good agreement is observed between the catalytic tests and the TPR experiments.

The Co catalyst also indicates a moderate CO selectivity in its presumably unreduced state (see Fig. 5). This may be caused by reforming of the primarily formed total oxidation products, or by Co giving a reasonably high primary selectivity to CO. After reduction at 950°C it shows good activity and selectivity in the CPO reaction at high temperature. Compared to the Ni-based catalyst, a rapid deactivation is observed during catalytic testing at temperatures below 550°C and equilibrium is not achieved. This is the type of properties that could be useful in a fluidized bed reactor, as discussed in the Section 1. However, the oxidation is obtained at a somewhat low temperature.

The actual state of Fe under reaction conditions could not be determined precisely. An increasing CO selectivity at temperatures above 900°C may suggest that a full reduction could be achieved at temperatures above 1000°C. This assumption agrees with the fact that some metallic Fe is obtained after reduction at 1000°C in the TPR experiments. The Fe-based catalyst may, therefore, be a possible CPO catalyst for a fluidized bed reactors at 1100°C. The poor methanation activity at low temperatures will then be an advantage.

5. Conclusion

Fe catalysts are clearly the most active catalyst for total oxidation by comparison with Ni- and Co-based ones. If problems are met with methanation reactions in the colder zones of a fluidized bed CPO process, Co- and possibly Fe-based catalysts may be interesting alternatives to traditional Ni-based catalysts. Fe catalysts will have to be investigated in the 1000–1100°C region to explore this potential.

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