**H2 production from partial oxidation of CH4 by Fe2O3-supported Ni-based catalysts in a plasma-assisted packed bed reactor**

**Yaoyao Zheng\*1, Rob Grant2, Wenting Hu3, Ewa Marek1 and Stuart A. Scott1**

*1Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, CB2 1PZ, United Kingdom.*

*2Gas Recovery & Recycle Ltd, Aztec House, Perrywood Business Park, Salfords, Surrey, RH1 5DZ, United Kingdom*

*3School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom*

\*Corresponding Author: yz450@cam.ac.uk

# **Abstract**

H2-rich gas production from CH4 at mild temperature (673 K), was achieved in a single step without introducing a separate oxygen stream. This was conducted in a plasma-assisted packed bed reactor in the presence of Ni-based catalysts doped on an active support, i.e. Fe2O3. Among the tested materials, NiO/Fe2O3 was found to be very promising and its excellent catalytic properties seemed to be induced by the presence of Fe2O3, which suppressed the formation of deposited carbon, and thus maintained the catalytic effect of metallic Ni (formed during NiO reduction by the CH4/Ar plasma). This work demonstrates the potential of plasma-assisted chemical looping partial oxidation for H2 production.

***Keywords***: plasma, chemical looping, H2 production, catalyst

# **Introduction**

Steam reforming of natural gas is used industrially for H2-rich gas production. The reforming reaction is endothermic and carried out at temperatures above 1073 K [1]. To improve the yield of H2, water-gas shift (WGS) is usually employed and operated at much lower temperatures (~ 673 K) due to the equilibrium constraints. Overall, the process is endothermic and external heating is needed. The fact that multiple stages are adopted in CH4-steam reforming makes it more appropriate for large scale processing and applications not requiring high purity H2.

Chemical looping H2 production, which employs solid oxygen carriers cycled between two interconnected reactors, has been actively studied due to its potential of achieving high yield and purity of H2 [2–4]. This technique usually requires high temperatures (~ 1073 K). For small- and medium-scale H2 production, suitable techniques also include water splitting (e.g. electrolysis) and plasma (particularly non-thermal) -assisted reforming processes [5]. Electrolysis is widely used but its significant electricity demand, high cost of catalysts, and the need to pretreat water, are issues [6]. In processes assisted by non-thermal plasma, H2 is produced at lower temperatures than would otherwise be possible [7–9]. CO2 or steam reforming of methane for H2 production in dielectric barrier discharge (DBD) reactors is one of the most attractive approaches [7]. To achieve a high yield of H2, the process often includes catalysts and Ni-based catalysts are commonly used due to their low cost and high catalytic activity. This, however, also implies short lifetime, as Ni-catalysts suffer from carbon deposition, and deactivation [10].

Here, a DBD reactor is used to achieve H2 production from CH4 at 673 K. In contrast to conventional plasma-assisted systems, an active oxygen carrier, Fe2O3, is proposed as the support for Ni-based catalyst. The introduction of Fe2O3 aims to provide a source of oxygen to suppress the carbon deposition, so that the activity of Ni could be maintained. The likely advantages of this plasma-assisted chemical looping H2 production (PCLH) approach are: (i) operating at low temperatures to favour selectivity for H2 and to reduce any downstream processing; ii) the chemical loop itself allows oxygen to be added to the process without a separate stream of oxygen.

# **Experimental**

## **Materials**

**Fe2O3-supported Ni-based materials**

Two Fe2O3-supported catalysts were prepared: NiO/Fe2O3 and NiFe2O4/Fe2O3. Pure Fe2O3 was also studied for comparison. Fe2O3 particles were prepared from iron oxide powders (Fisher Scientific; 10 , > 95 wt%) by granulation, using de-ionised (DI) water (1/10th the mass of Fe2O3), as a binder. After mixing, the resulting granules were sieved to 600 – 1000 , then calcined at 1273 K for 6 hours in air. The sintered particles were re-sieved to 600 – 850 . The Ni-based Fe2O3-supported materials were then prepared by dry-impregnation. Nickel nitrate hexahydrate (Sigma-Aldrich, Ni(NO3)26H2O, 98.5 %), was mixed with the Fe2O3 particles, followed by the addition of DI water to just dissolve the nitrate. The resulting mixture was stirred at 313 K for 20 min, followed by drying at 398 K for 12 hours. The dried mixture was then calcined at 823 K for 5 hours to form NiO/Fe2O3, or at 1123 K for 5 hours to produce NiFe2O4/ Fe2O3. In both cases, the molar ratio of Ni to the total metal (i.e. Ni + Fe) was about 1: 10.

**Al2O3-supported Ni-based materials**

As a control, materials were also prepared with Al2O3 instead of Fe2O3. The preparation of Al2O3 started with aluminium oxide pellets (Sigma-Aldrich, -Al2O3, 3 mm). The pellets were crushed to 600 – 850 , and then calcined at 1273 K for 6 hours in air. The preparation of NiO/Al2O3 followed the same protocol (i.e. dry-impregnation) as that for NiO/Fe2O3. The prepared NiO/Al2O3 was then divided into two equal portions. One portion was used as prepared, i.e. NiO/Al2O3. The other portion was reduced at 1073 K in 5 % H2 (balance N2, BOC) for 30 min to obtain Ni/Al2O3. Similarly, the resulting Al2O3-supported Ni-based particles had a sieve size of 600 – 850 , with a Ni to total metal molar ratio of 1: 10.

## **Apparatus**

The DBD reactor (Fig. 1) was made of a quartz tube (i.d. 25.0 mm, o.d. 28.0 mm), acting as the packed bed reactor as well as the dielectric material between the two electrodes. A co-axial stainless-steel rod (diameter of 12.0 mm) within the quartz tube formed the high voltage electrode. A stainless-steel mesh wrapped around the outer surface of the quartz tube formed the ground electrode, enclosing a height of 20 mm. The gap between the quartz tube and the high voltage rod surface (6.5 mm) was the plasma discharge zone and was packed with the prepared materials (a volume of 7.5 ml). The system was operated at atmospheric pressure and heated externally with its temperature measured by a K-type thermocouple (positioned outside the DBD reactor, the temperature inside the bed was about 5 K higher). AC power (primary) was supplied to the DBD reactor with a voltage of 10.5 1.0 kV and frequency 26.0 3.0 kHz(PVM500-2500, Information Unlimited). The dissipated plasma power (determined by Q-V Lissajous plot) was controlled at 7.2 0.7 W.

The gas stream entered the DBD reactor from the bottom at 0.75 L/min (all the flow rates are expressed at 293 K and 1 atm), low enough to prevent fluidisation. The product gas was sampled at 0.5 L/min. H2 and O2 were measured by a thermal conductivity analyser (ABB, Caldos27) and a paramagnetic oxygen analyser (ABB, magnos206), respectively. Carbon-containing gas species were measured by a Fourier transform infrared (FTIR, MKS Instruments - MultiGasTM) analyser. For a typical experiment, the reactor was heated to 673 K in flowing air (BOC, 99.995%), followed by Ar (BOC, 99.998%) to purge the system before the start of the experiment. During an experiment, a stream of CH4 (BOC, 99.5%) was mixed with Ar to give 8.5 0.5 vol% CH4. After the mixed gas flow stabilised, the plasma was applied. For each experiment, the plasma discharge period was about 5.6 0.5 min. After CH4/Ar plasma discharge, the gas was switched to air to burn off any deposited carbon as well as re-oxidise the bed materials. Plasma discharge was later introduced to assist the process of de-coking and re-oxidation. The reduction-oxidation cycle was repeated three times.

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Figure 1 Illustration of the DBD reactor.

## **Data analysis**

The main gaseous products observed were H2, CO, CO2, with traces of C2H2, and C2H4 (< 150 ppm). The averaged conversion of CH4, , is defined as:

= ,

where and are CH4 mole fractions measured at the reactor inlet and outlet, respectively. and are the corresponding total flow rates. The converted CH4 was averaged for the period with plasma discharge. Assuming that the amount of Ar did not change over time, only CO, CO2, H2, C2H2, C2H4 and Ar were present at the outlet, then the total flow rate at the outlet (dry basis), , can be obtained from the Ar balance:

.

The averaged selectivities, for CO or CO2, and for H2, are given as:

=

= ,

where is based on C in CH4, and is based on H in CH4.

The average yield for each product, , was defined as the amount of component *i* produced for every mole of CH4 introduced into the DBD reactor:

.

The fraction of carbon deposited was estimated from the difference between the carbon input and that detected at the outlet during the reduction period:

.

The carbon and hydrogen balances were also estimated, and defined as the ratio of carbon/hydrogen-containing species measured to the carbon/hydrogen in the converted CH4 in a complete looping cycle (i.e. CH4/Ar plasma discharge followed by air plasma discharge stage).

# **Results**

## **Al2O3 and Fe2O3**

The results of plasma-assisted cracking or/and partial oxidation of CH4 in undoped Al2O3 and Fe2O3 beds are presented in Fig. 2. For both materials, CH4 conversion was only observed when plasma discharge was applied. H2 was found to be the main product and its generation over the discharge was relatively uniform. CO and CO2 were observed only at trace levels (< 250 ppm). This suggests that H2 was primarily generated from CH4 cracking by the plasma, and the carbon from the converted CH4 deposited onto the solid phase. This agrees with the fact that the ratio of generated H2 to converted CH4 was 1.7 0.1 (based on three cycles) for both materials. Taking into account C2H2 and C2H4 generated during discharge period (at ppm levels), over 80 % hydrogen balance was obtained for both materials (see Table 1). The conversion of CH4, as well as the generation of H2, in the Al2O3 and Fe2O3 beds were similar, suggesting that neither material is a good catalyst for CH4 cracking. In the air plasma discharge period, trace levels (< 100 ppm) of CO and CO2 were observed, suggesting the presence of deposited carbon from the cracking process in the bed. However, the deposited carbon could not be removed completely at such low temperatures, even with the assistance of plasma. Further regeneration of the bed was carried out by raising the temperature of the reactor to 823 K for over 30 min until no CO and CO2 were detected.

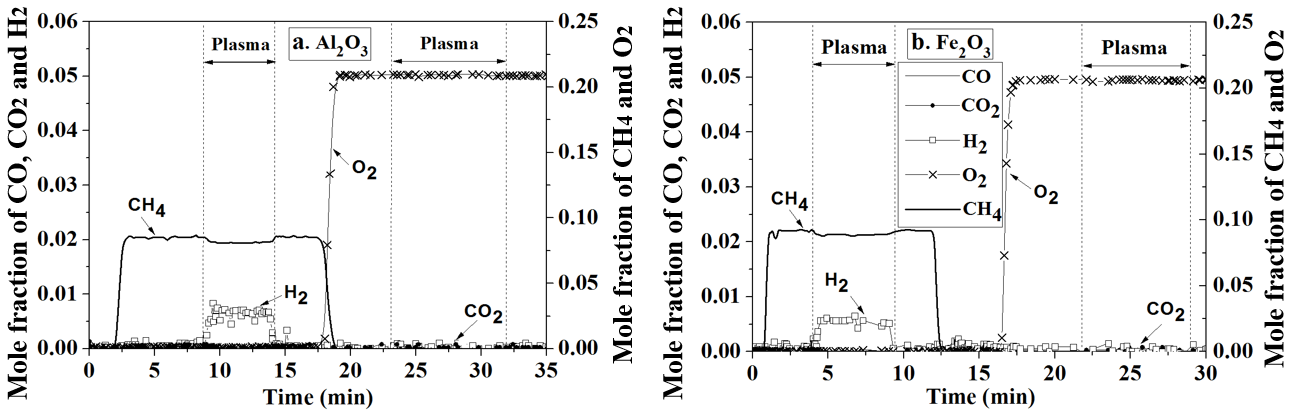


Figure 2 Plasma-assisted cracking/partial oxidation of CH4 at 673 K with DBD reactor packed with a) Al2O3; b) Fe2O3.

## **NiO/Al2O3, Ni/Al2O3, NiO/Fe2O3 and NiFe2O4/Fe2O3**

CH4 conversion in the NiO/Al2O3 bed, shown in Fig. 3a, was similar to those in Al2O3 and Fe2O3 beds, suggesting that this material also has little effect on CH4 reforming or partial oxidation. For Ni/Al2O3 as seen in Fig. 3b, a significant rise in [H2] was observed when CH4 was introduced into the reactor, without plasma. This was mainly due to the catalytic effect of Ni, as reported in e.g. ref [10]. However, the catalytic effect did not last long and the H2 level dropped and gradually reached a mole fraction of 0.01, whilst no significant production of CO and CO2 was observed. This suggests that the deactivation of Ni was likely due to carbon deposition. The formation of nickel aluminate (confirmed by post-reaction XRD results shown in Fig. S1) could have also contributed to this deactivation. When plasma discharge was applied from *t* = 9.5 to *t* = 15.6 min, higher degrees of CH4 conversion and H2 production were achieved. At *t* = 22.0 min, CH4 was stopped, leaving the bed purging in Ar. Then, as soon as the gas was switched from Ar to air, a significant CO2 peak together with a small CO peak was observed and an overall carbon balance of 94% was obtained.

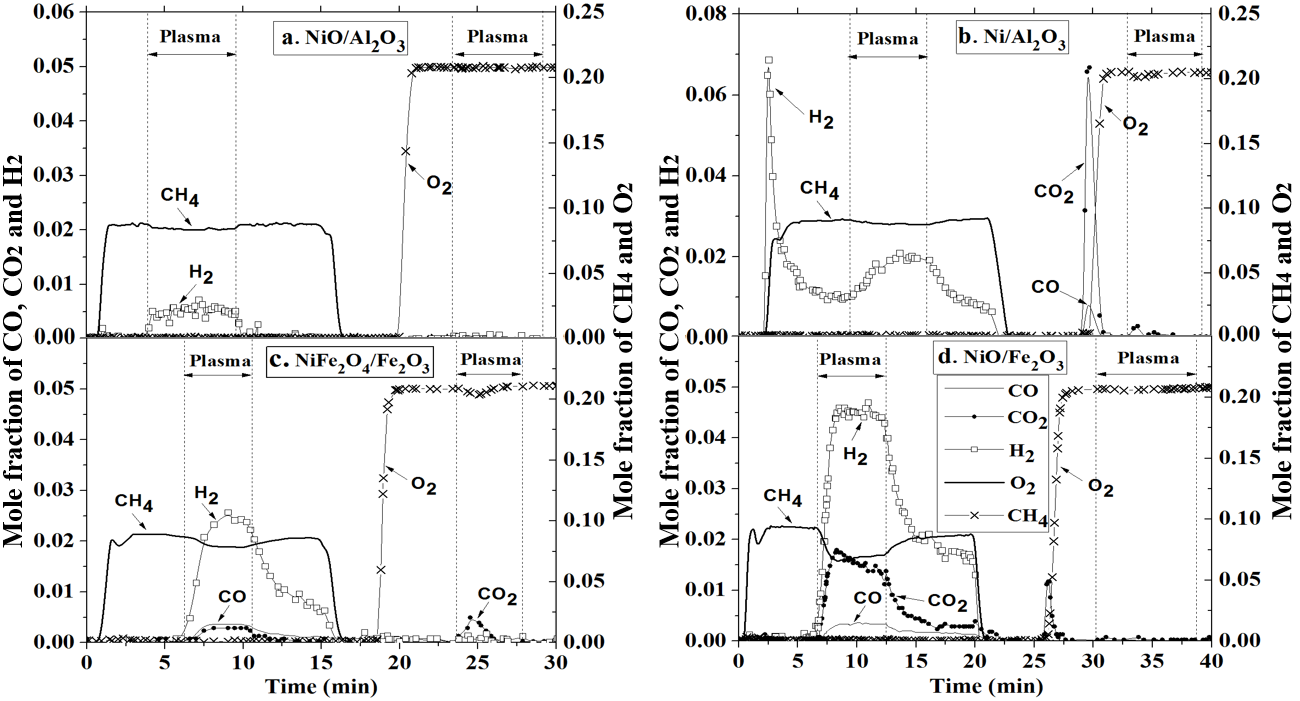


Figure 3 Plasma-assisted cracking/partial oxidation of CH4 at 673 K with DBD reactor packed with a) NiO/Al2O3; b) Ni/Al2O3; c) NiFe2O4/Fe2O3; d) NiO/Fe2O3.

When the reactor was loaded with NiFe2O4/Fe2O3, according to Fig. 3c, no significant conversion of CH4 was seen without plasma discharge. At *t* = 6.8 min, when plasma was introduced, much improved generation of H2 over the whole discharge period was observed; at the same time, there was a clear production of CO and CO2, indicating that the reduction of the bed material occurred (NiFe2O4/Fe2O3 was the only source of oxygen in the system). The overall result was a partial oxidation of CH4 by plasma discharge to a product stream rich in H2, CO and CO2. When plasma discharge was stopped, H2 was still produced from the NiFe2O4/Fe2O3 bed, though at lower levels. The fact that NiFe2O4 was not reactive for H2 production before plasma discharge but was after, suggests the generation of some additional phase other than NiFe2O4 during plasma discharge, with this (probably reduced) phase having a catalytic effect even without plasma. In the air regeneration stage, CO2 was only observed when plasma was applied. In the NiO/Fe2O3 bed, according to Fig. 3d, no conversion of CH4 was observed until plasma was applied, at which point a significant amount of H2 was generated. The CO and CO2 productions were also much higher than those from other beds during plasma discharge. CH4 conversion reached 32% in this instance. Similar to the case in the NiFe2O4/Fe2O3 bed, when plasma was switched off, there was still post-plasma H2 production. Most of the deposited carbon was recovered in air, without the presence of plasma. It should be noted that it was not possible to prepare and investigate Ni/Fe2O3 because Ni/Fe2O3 is thermodynamically unstable at the studied conditions.

Table 1 Summarised results in different bed materials (errors show the range of three repeats).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Parameters** | **Al2O3** | **NiO/Al2O3** | **Ni/Al2O3** | **Fe2O3** | **NiO/Fe2O3** | **NiFe2O4/ Fe2O3** |
|  | 0.75 0.04 | 0.75 0.03 | 0.90 0.07 | 0.71 0.05 | 0.15 0.03 | 0.47 0.08 |
| **C balance** | 0.26 0.02 | 0.25 0.02 | 0.94 0.02 | 0.38 0.02 | 0.94 0.03 | 0.63 0.04 |
| **H balance** | 0.93 0.04 | 0.94 0.03 | 0.96 0.04 | 0.82 0.02 | 0.82 0.03 | 0.99 0.06 |
|  | 0.05 0.01 | 0.05 0.01 | 0.10 0.02 | 0.04 0.01 | 0.39 0.07 | 0.19 0.04 |
|  | 0.01 0.01 | 0.01 0.01 | 0.03 0.01 | 0.01 0.01 | 0.12 0.01 | 0.25 0.01 |
|  | 0.03 0.01 | 0.06 0.01 | 0.02 0.01 | 0.08 0.01 | 0.71 0.02 | 0.27 0.02 |
|  | 0.84 0.01 | 0.85 0.01 | 0.95 0.01 | 0.74 0.01 | 0.92 0.01 | 0.98 0.07 |
| **×103** | 0. 3 0. 1 | 0.3 0.1 | 0.3 0.1 | 0.2 0.1 | 45.2 4.9 | 38.4 5.2 |
| **×103** | 1.2 0.3 | 2.7 0.5 | 2.2 0.6 | 3.2 0.7 | 285.5 15.1 | 45.4 3.1 |
| **×103** | 64.7 1.4 | 81.3 1.2 | 180.6 11.2 | 58.9 1.1 | 621.7 32.3 | 319.0 40.2 |

Table 1 presents the summarised results of degree of carbon deposition, conversion of CH4, selectivity and yield for products, carbon and hydrogen balances. It should be noted that after three cycles, no mechanical deterioration was visually observed for any of the tested materials. Overall, NiO/Fe2O3 seems to be the most promising material for H2 production due to its low degree of carbon deposition, high carbon and hydrogen balances, and high selectivity and yield for H2. The hydrogen balance in the case of NiO/Fe2O3 was slightly lower than those in other Ni-doped materials. This suggests that some H-containing products other than H2 might have been generated, probably H2O. NiFe2O4/Fe2O3 also exhibited very high selectivity towards the production of H2, although its resistance to coking, carbon balance and the conversion of CH4 were not as good as those of NiO/Fe2O3.

## **XRD results for NiO/Fe2O3 and NiFe2O4/Fe2O3**

To evaluate any possible change in the material structure after the plasma-assisted CH4 conversion, the bed material samples were collected and X-ray powder diffraction (XRD) performed using an Empyrean PANalytical diffractometer. A typical diffractogram was collected in the range of from to using Cu radiation with a voltage of 40 kV and current of 40 mA. The phases in the samples were identified using the reference patterns from ICSD database (Table S1).

### **NiO/Fe2O3**

Figure 4 shows the XRD patterns of NiO/Fe2O3 samples: freshly prepared, with CH4/Ar plasma treatment and after regeneration in air plasma. Major peaks of each phase and an unknown peak ( = 26.7) are marked accordingly. For the freshly calcined NiO/Fe2O3, only NiO and Fe2O3 were detected. This suggests no chemical interaction between NiO and Fe2O3 during calcination. After CH4/Ar plasma treatment, NiO was no longer detected; instead, metallic Ni and magnetite, Fe3O4, were detected. For the air regenerated NiO/Fe2O3, similar to the fresh sample, NiO and Fe2O3 were the only phases detected, suggesting that the NiO phase can remain separate during plasma discharge in air.

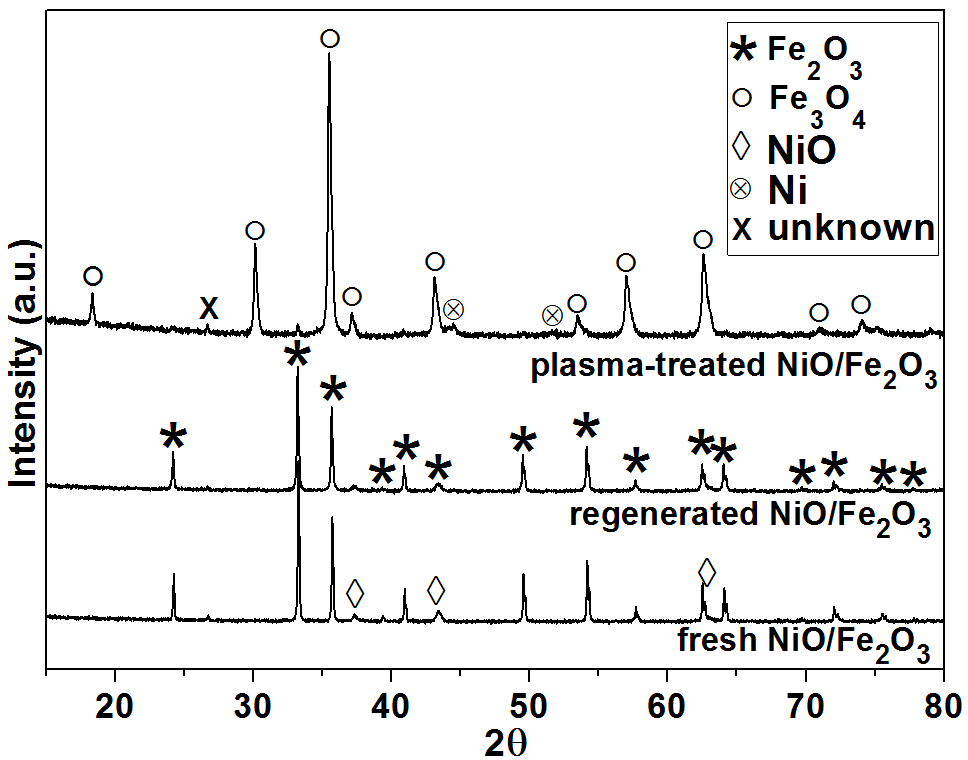


Figure 4 XRD spectra of fresh NiO/Fe2O3, CH4/Ar plasma treated NiO/Fe2O3 and air plasma regenerated NiO/Fe2O3.

### **NiFe2O4/Fe2O3**

XRD Results for NiFe2O4/Fe2O3 samples are presented in Fig. 5. Fe2O3 and NiFe2O4 phases were observed in the fresh sample. The formation of NiFe2O4 indicates the diffusion of NiO into the Fe2O3 crystal structure during calcination. In the XRD pattern of the CH4/Ar plasma treated NiFe2O4/Fe2O3, there was a decrease in the intensity of the peaks for the NiFe2O4 phase; additionally, metallic alloy of Ni-Fe, expresses as (Ni, Fe), was observed. There was no clear evidence of the presence of Fe3O4, suggesting that the oxygen in the produced CO and CO2 in the CH4/Ar discharge period probably came from the reduction of NiFe2O4 to the metallic (Ni, Fe). On regeneration with air, the (Ni, Fe) phase disappeared, but the intensity of NiFe2O4 peaks did not return to the higher level as seen in the fresh NiFe2O4/Fe2O3 sample.

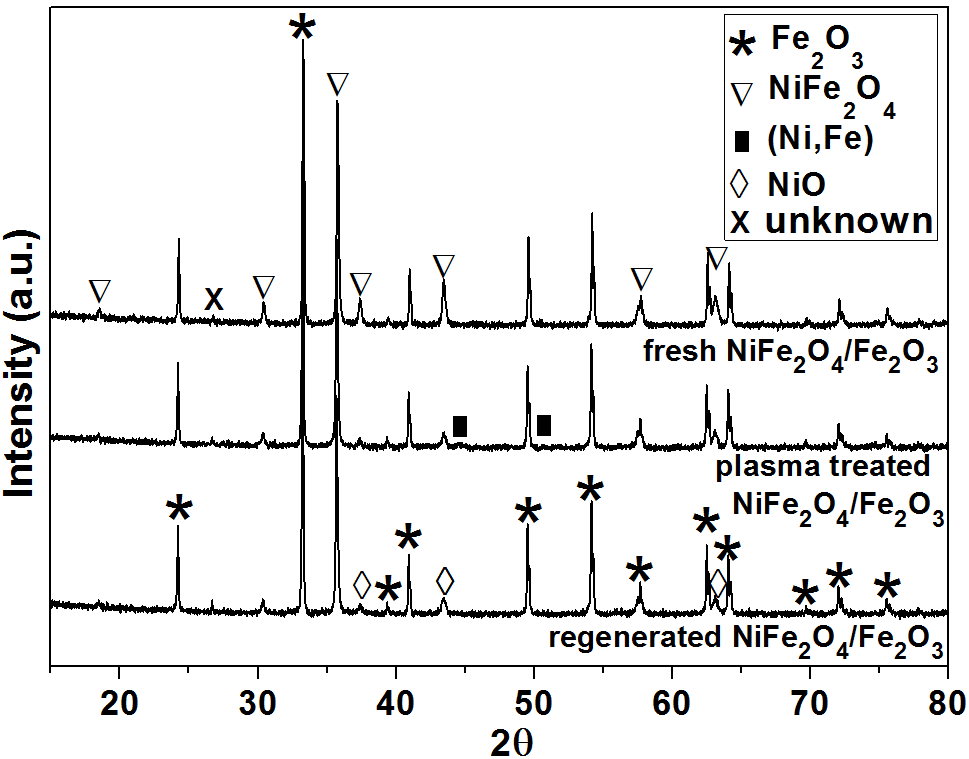


Figure 5 XRD spectra of fresh NiFe2O4/Fe2O3, CH4/Ar plasma treated NiFe2O4/Fe2O3 and air plasma regenerated NiFe2O4/Fe2O3.

# **Discussion**

## **Catalytic activity**

The results in Figs. 2 and 3 show that NiO (when supported on inert Al2O3) and Fe2O3 alone did not show good catalytic activity for the conversion of CH4, even in the presence of the plasma discharge. However, the combination of NiO and Fe2O3, which resulted in NiO/Fe2O3 or NiFe2O4/Fe2O3, demonstrated significantly improved performance.

### **NiO/Fe2O3**

The results in Fig. 4 imply the formation of Ni when NiO/Fe2O3 was subjected to CH4/Ar plasma discharge. In contrast to the Ni/Al2O3 experiment (in Fig. 3b), where the production of H2 was high at the very beginning of the plasma discharge but decreased quickly, the bed of NiO/Fe2O3 was able to produce significant amounts of H2 over the entire plasma discharge period. The superior performance of NiO/Fe2O3 might have resulted from lattice oxygen in NiO/Fe2O3, which seems to suppress the coking of the solid bed, so that the catalytic activity of Ni can be maintained. This is supported by the smaller amount of carbon deposited in the NiO/Fe2O3 bed. Owing to the presence of Fe3O4, it was difficult to determine if NiO was still present in the plasma treated NiO/Fe2O3 sample from the XRD (NiO peaks overlap with those from Fe3O4). However, calculation of the oxygen balance can provide additional insight on to the phases present. It was found that the amount of oxygen in the produced CO, CO2 and H2O (estimated from the hydrogen balance) during CH4/Ar plasma discharge period accounted for 3.2 wt% 0.2 wt% of the total mass of NiO/Fe2O3. The oxygen capacity from NiO Ni was 2.0 wt%, whilst that in Fe2O3 Fe3O4 was 3.0 wt%. As most of the hematite was reduced (only low intensity of Fe2O3 peaks were detected), it is possible that some NiO might have remained after CH4/Ar plasma discharge.

Interestingly, the NiFe2O4 phase was not observed in the XRD pattern of the NiO/Fe2O3 (Fig. 4), suggesting little interaction between NiO and Fe2O3, either during calcination or plasma treatment. The fact that NiO alone was inactive during plasma discharge, suggests the presence of some available oxygen in the NiO/Fe2O3 to suppress coking. One of the three hypothesis might describe these conditions: 1) NiO itself is responsible for the partial oxidation of CH4 *via* NiO + CH4 CO + CO2 + H2 + Ni, and Fe2O3 helps the process to continue by transporting oxygen to the Ni sites; 2) metallic Ni is responsible for the generation of H2 *via* CH4 C + H2, and the presence of Fe2O3 helps to remove the solid carbon from the Ni sites; 3) a combination of 1) and 2). The above results seem to suggest that 2) is more likely to dominate, as the H2 production rate in the NiO/Fe2O3 bed was comparable to that when Ni/Al2O3 was just exposed to CH4. This is further supported by the results from SEM-EDX analysis, which showed that the surface of NiO/Fe2O3 particles treated with CH4/Ar plasma was predominantly covered by Ni (see Fig. S2 and Table S2). Furthermore, the trace amounts of CO and CO2 produced from NiO/Al2O3 subjected to CH4/Ar plasma discharge were similar to those from bare Al2O3 and Fe2O3 beds, showing that NiO in the absence of Fe2O3 cokes easily, or does not react with CH4.

It is reasonable to identify the sequence of phase transformation of NiO/Fe2O3 in the reducing CH4 environment by referring to the Ni-O and Fe-O phase diagrams (computed by MTDATA [11], see Figs. S3 and S4). Thermodynamically, at 673 K, the to cause a phase transition from NiO to Ni is lower than that for Fe2O3 to Fe3O4, but higher than that for Fe3O4 to Fe. This means that assuming negligible solubility of NiO into the Fe2O3 system, the sequence for reduction would be: Fe2O3 + NiO NiO + Fe3O4 Ni + Fe3O4. Therefore, in a reducing environment, it is expected that if Ni was detected, Fe3O4 would then also be present. However, at the relatively mild temperatures in this study, reaction kinetics are important and Fe2O3 is un-reactive towards CH4. A high level of H2 production in NiO/Fe2O3 was observed as soon as the plasma discharge was applied. If the catalytic effect for H2 production was only due to the presence of metallic Ni, then the formation of Ni must have happened as soon as NiO/Fe2O3 was subjected to plasma discharge. This contrasts with the pure NiO/Al2O3 material, which could also have reduced to Ni locally, but for some reason remained inactive, perhaps because of coking, with carbon immediately deposited on any newly created Ni-metallic site. Additionally, the formation of nickel aluminate after plasma treatment also means that less Ni was available for CH4 cracking. If Ni formed immediately when plasma was applied in the NiO/Fe2O3 bed, the suppression of coking was most likely due to the presence of an oxygen source, i.e. Fe2O3. The co-existence of Ni and Fe2O3 is thermodynamically unstable, and the system tends to form NiO and Fe3O4 at equilibrium. The transfer of oxygen to the Ni sites would then help remove any deposited carbon, or prevent transiently formed absorbed carbon species from forming coke, and thus maintaining the catalytic activity of Ni. This means that a synergistic effect, which here most likely depends on the CH4, Ni and oxygen from Fe2O3 being in intimate contact, exists. For NiO/Fe2O3, not only was less coke formed, but also the remaining coke was more easily burned off during the air regeneration stage, compared with other materials e.g. NiO/Al2O3 and Fe2O3. The superior performance of the NiO/Fe2O3 for H2 production and its easy regeneration demonstrate the possibility of plasma-assisted chemical looping system for H2 production at mild temperatures. The process requires further studies and careful optimisation. Interestingly, at higher temperatures, as observed in preliminary tests at 773 K, plasma treatment on NiO/Fe2O3 resulted in total combustion of CH4 to H2O and CO2.

### **NiFe2O4/Fe2O3**

As shown in Fig. 4, the observed (Ni, Fe) phase together with the decreased intensity of NiFe2O4 peaks in the XRD spectra in the CH4/Ar plasma treated sample, indicates the phase segregation of NiFe2O4 to (Ni,Fe). This seems to be consistent with the study carried out by Raghavan [12]. At 1273 K and low ( < 10-11 bar)**,** NiFe2O4 tends to reach equilibrium with (Ni, Fe)3O4 and (Ni, Fe). Extrapolating to the low temperatures used here, it is reasonable to expect that the reduction follows NiFe2O4 (Ni, Fe)3O4 + (Ni, Fe). In our study, when the NiFe2O4 material was regenerated in air plasma at 673 K (Fig. 5), the (Ni, Fe) peaks disappeared. The most likely route for Ni oxidation is to create NiO. However, the presence of NiO was difficult to confirm, due to significant overlap of the NiO and NiFe2O4 peaks in the XRD pattern. For Fe, no evidence of wustite or magnetite phase was observed, and the most likely route would then be Fe Fe2O3. In terms of the catalytic effect in the NiFe2O4 bed, it was found that H2 yield improved slightly in the second and third reduction cycles (Fig. S5). If NiO was indeed created in the regeneration stage, then it could have helped with the production of H2 in subsequent reductions.

## **Comparison to water gas shift equilibrium**

In NiO/Fe2O3, the products from CH4/Ar plasma discharge were mainly H2 and CO2. A high yield of H2 and CO2 at such low temperature (673 K) could be linked with WGS (H2O + CO H2 + CO2). Assuming that water was also produced and is responsible for the missing H in the mass balance (as shown in Table 1), then the reaction quotient, = 64.6 19.1, can be compared with the equilibrium constant of WGS at 673 K, *Keq* = 12.0 [13]. This suggests that the plasma-assisted process tends to push production of H2 and CO2, beyond the thermodynamic equilibrium of WGS. To achieve a *Keq* close to the reaction quotient obtained here, the conventional WGS would need to operate at a lower temperature (though it should be noted that excess water is usually used to shift the equilibrium). For the WGS to achieve a high conversion to H2 and maintain favourable kinetics, multiple reaction stages are often employed (e.g. moving from high to low temperatures), and thus complicating the process. For the presented PCLH approach, the fact that such high production of H2 and CO2 was achieved within such a small bed (~ 7.5 ml) indicates fast reaction rates. The high value of found here seems to suggest that H2 and CO2 might be directly produced from the partial oxidation of CH4 by the oxygen carrier, without going through some intermediate steps involving WGS. The unusually high ratio is likely to be a result of H2 and CO2 not having sufficient time to reach a WGS equilibrium.

## **4.3 Energy cost for H2 production**

Assuming electricity production from CH4 combustion with 60% efficiency (see supplementary information Eq. S1), the estimated energy cost for H2 production from a NiO/Fe2O3 bed, is 440 20 MJ/kg of produced H2 (based on HHV of CH4). This is higher than the cost of conventional steam methane reforming, which is less than 160 MJ/kg [14], but comparable to that of water electrolysis, from 320 to 510 MJ/kg (estimated based on electricity consumption between 50 to 79 kWh/kg [15]). Given that the current experimental set-up can be further optimised, there is scope for further cost reduction.

# **Conclusions**

Ni-based catalysts supported on Al2O3 and Fe2O3 were investigated for plasma-assisted H2 production from CH4. Experiments carried out in a DBD packed bed reactor at 673 K showed that the supporting metal oxide, Fe2O3, positively influences the activity of the catalyst. Among the tested materials, NiO/Fe2O3 exhibited the highest H2 yield, whilst carbon deposition and the subsequent catalyst deactivation were significantly lower than those from NiO or Ni supported on alumina.

The catalytic activity for H2 production in the combined catalyst/oxygen carrier (NiO/Fe2O3) was attributed to the generation of metallic Ni, and the suppression of carbon deposition was connected to the presence of the active metal oxide, Fe2O3. The hydrogen yield form the plasma-assisted CH4 reforming and oxidation by the oxygen carrier exceeded that anticipated from the WGS equilibrium.

# **Acknowledgements**

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**List of supplemental materials**

**Fig. S1** XRD spectra of CH4/Ar plasma treated NiO/-Al2O3. Material was only reduced and not regenerated with air after the plasma treatment.

**Fig. S2** SEM micrograph combined with EDX analysis of NiO/Fe2O3 particle surface after experiment in the DBD reactor. The material was retreated after CH4/Ar plasma-assisted reduction (no air regeneration). The micrograph was collected with TESCAN MIRA3 FEG-SEM combined with Oxford Instruments Aztec Energy X-maxN 80 EDS system at an accelerating voltage of 15 kV, working distance of 14 mm and 1000x magnification. The quantitative results from the EDX analysis are presented in Table S2.

**Fig. S3** Phase diagram of Ni-O system, calculated with MTDATA [11] (SGTE database).

**Fig. S4** Phase diagram of Fe-O system with MTDATA [11] (NPL database).

**Fig. S5** H2 concentration measured during three subsequent CH4/Ar plasma discharge experiments, using NiFe2O4/Fe2O3 as the bed material.

**Table S1** Collection Code of the XRD reference patterns used from ICSD database.

**Table S2** Results from the EDX analysis of NiO/Fe2O3 particle surface after experiment in the DBD reactor. The material was retreated after CH4/Ar plasma-assisted reduction (no air regeneration). The analysis was performed with TESCAN MIRA3 FEG-SEM combined with Oxford Instruments Aztec Energy X-maxN 80 EDS system at an accelerating voltage of 15 kV, working distance of 14 mm and 1000x magnification. The SEM micrograph and EDX maps are presented in Fig. S2.

**Eq. S1** The energy cost for H2 production, MJ /kg.

**Fig. S1**



**Fig. S2**



**Fig. S3**



**Fig. S4**



**Fig. S5**



**Table S1**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Component** | Fe2O3 | Fe3O4 | NiO | Ni | NiFe2O4 | (Ni, Fe) | NiAl2O4 |
| **Collection Code from ICSD** | 15840 | 30860 | 9866 | 260169 | 40040 | 56386 | 9556 |

**Table S2**

|  |  |  |
| --- | --- | --- |
| **Element** | **Weight in wt%** | **in wt%** |
| C | 6.59 | 0.06 |
| O | 10.84 | 0.03 |
| Fe | 20.28 | 0.05 |
| Ni | 62.2 | 0.07 |

**Eq. S1**

The energy cost in this manuscript was defined as:

Energy cost = ,

where W is the applied plasma power, is the amount of H2 produced over processing time. is the chemical exergy of CH4, which is ~ 52 MJ/kg. is the efficiency from thermal to electricity energy and a value of 60% is assumed here. is the converted amount of CH4, and is the high heating value of (~ 55.5 MJ/kg).