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The oxidative chemistry of methane over supported nickel catalysts

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Abstract

The oxidative chemistry of methane over nickel catalysts dispersed on silica, alumina, titania, ceria and zirconia supports has been studied. Temperature programmed reduction (TPR) has been used to study the reduction characteristics of the catalysts. These measurements reveal the presence of two distinct types of nickel oxide, which are reduced at significantly different temperatures on the different catalysts. The activity for methane conversion and selectivity towards partial oxidation has been studied as a function of reaction temperature using temperature programmed reaction spectroscopy (TPRS). Ni/SiO_2 showed the highest activity and selectivity towards CO formation. At 1160 K the selectivity towards CO formation varied from 85% for Ni/SiO_2 down to 29% for Ni/Al_2O_3. In addition, the transient activity of a partially reduced Ni/CeO_2 catalyst and non-reduced Ni/SiO_2 and Ni/TiO_2 catalysts have been studied. The temperature at which methane activation occurs on the different catalysts has also been examined. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Nickel; Partial oxidation; Methane conversion; Syngas; Temperature programmed measurements

1. Introduction

The conversion of natural gas which contains mostly methane to value-added products, such as easily transportable fuels, is driven by the tremendous abundance of natural gas in remote areas, as well as other economic factors. The energy per unit volume of natural gas is much lower than that of liquid fuels [1], and this coupled with the gaseous state and low boiling point make methane very expensive to transport by methods involving liquefaction or via pipeline [2]. Thus, in recent years the direct and indirect conversion of methane to value-added products has attracted a great deal of attention [3–8].

We have an additional interest in the catalytic chemistry of methane which relates to solid oxide fuel cells (SOFCs). Fuel cells have tremendous potential as a more efficient and cleaner alternative method of electricity generation than conventional methods [9]. The SOFC is the ideal device for small-scale application, offering the potential of cheap, clean production of electrical power from natural gas, because it operates at temperatures between 1023 and 1273 K where methane reacts readily with oxygen or steam [10]. The possibility of internal conversion of methane directly on the anode surface is one of the main benefits of the SOFC compared to other fuel cell systems. However, this presents considerable practical difficulties not least since the anode must function as both an active methane conversion catalyst and as an efficient electrode in intimate contact with the solid electrolyte. Consequently, several major problems of internal conversion of methane remain to be solved before SOFCs which run on methane (or higher hydrocarbons) can ever be routinely used, in particular that of carbon deposition and poor durability in opera-

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tion. Under normal operating conditions significant coking of the anode occurs when the cell is run on methane. This can be reduced by adding steam to the fuel or potentially by the addition of additives to the catalyst. However, although the addition of steam to the fuel may be beneficial for the removal of carbon deposits, it is somewhat undesirable in fuel cell operation, as addition of oxygen ions to the anode side of the electrolyte reduces the electrical potential; the addition of steam to the cell also introduces major additional design considerations. In the working fuel cell, there is a flux of oxygen ions through the electrolyte to the anode, which can then react with methane at the anode surface, providing an additional route for methane conversion.

Since we have a particular interest in the development of SOFCs which can run on natural gas, as well as in the general area of natural gas conversion, we are undertaking a detailed investigation of the catalysis and surface chemistry which result from the addition of oxygen to methane; namely partial and total oxidation and oxidative coupling. We are concentrating our study on supported nickel catalysts, since in addition to being active for methane conversion [11], most SOFCs currently use a nickel-based anode [9].

There have been several studies published recently on the partial oxidation of methane over supported metal catalysts. Ru has been reported as having an exceptionally high activity and selectivity [3]. Other studies have also been carried out on Rh, Pd and Pt [12] catalysts, as well as on nickel catalysts [7,8,12–14]. It has been reported that high yields and high selectivities towards syngas can be obtained over supported nickel catalysts at relatively low temperatures [7,8,14].

In this paper, we have studied the oxidative chemistry of methane over nickel catalysts dispersed on silica, alumina, titania, ceria and zirconia supports. The catalysts have been characterised using temperature programmed reduction (TPR). The surface reactions between methane and oxygen on the different catalysts have been studied using temperature programmed reaction spectroscopy (TPRS). Temperature programmed oxidation (TPO) has been used to characterise the nature and quantity of the surface carbon formed on the catalyst surface during reaction. In particular, the partial oxidation of methane has been studied as a function of reaction temperature. In this paper, we focus on the behaviour at relatively low oxygen partial pressures, since this most closely resembles the situation encountered in a working SOFC where the flux of oxygen ions through the zirconia electrolyte is relatively small. In addition to studying the catalysis and surface chemistry on the reduced nickel catalysts, the activity and selectivity of the catalysts in partially reduced and non-reduced states have also been investigated.

2. Experimental

All the experiments described here were carried out on a custom-built catalytic flow reactor, which can be used to perform TPRS as well as conventional catalytic measurements. The essential components of the apparatus are a ceramic furnace which is operated by a Eurotherm temperature controller which allows the heating rate to be linearly controlled between room temperature and 1373 K; heating rates of between 1 and 20 K min^{-1} are possible. The reactor temperature is measured using a K-type thermocouple. The reactor inlet is linked to a stainless-steel gas manifold which allows complete flexibility in gas handling; helium is used both as a carrier gas for the reactant stream and as an inert flow for the reactor bypass system. The flow of helium, hydrogen and oxygen is controlled by needle flow-control valves, whilst the methane flow is controlled by a mass flow controller (Unit Instruments). Water was removed from gas stream using 13X molecular sieve traps. The gas manifold has been designed in such a way that gas mixtures of any combination and ratio can be achieved. A 4-way sampling valve (Whitey) placed before the reactor inlet can be used to divert reactant gases through the bypass system, allowing reactant gas composition to be changed whilst maintaining the reactor under a continuous flow of helium. Either a stainless-steel or quartz reactor can be employed. The exit from the reactor is connected to the gas analysis system, which is heated to 383 K to avoid the problem of water condensation. Gas analysis is carried out by an on-line computer-interfaced mass spectrometer (Leda-Mass Satellite).

All nickel catalysts were prepared by incipient wetness impregnation of nickel(II) nitrate (Fluka) onto the appropriate support (SiO_2, Al_2O_3, TiO_2, ZrO_2, and CeO_2). All catalysts had a nickel loading of 5% by weight. Following preparation the catalysts were dried at 403 K in an air oven overnight. The catalysts were calcined in a 8% O_2/He stream at 873 K for 1 h prior to TPR experiments. For partial oxidation experiments all samples which were used in the fully reduced state were treated in a 10% H_2/He stream at 953 K for 1 h, apart from Ni/CeO_2 which was reduced at a higher temperature of 1073 K. Ni/CeO_2 which was studied in the partially reduced state was reduced for 1 h at 728 K before use.

TPR measurements were carried out in a 10% H_2/He mixture using a heating rate of 5 K min^{-1}. The TPRS measurements described were carried out using a methane/oxygen ratio of 4:1 and a heating rate of 5 K min^{-1}. TPO experiments were carried out using an 8% O_2/He mixture and a heating rate of 5 K min^{-1}. All products formed during TPR, TPRS and TPO were analysed using on-line mass spectrometry. The mass spectrometer was capable of analysing 12 masses per second and the following masses were used to identify products: 2 – hydrogen, 4 – helium, 15 – methane, 18 – water, 27 – ethylene, 28 – carbon monoxide, 30 – ethane, 32 – oxygen, and 44 – carbon dioxide.

3. Results

3.1. Temperature programmed reduction

Following the calcination method outlined in Section 2 the supported nickel catalysts were characterised using (TPR); a heating rate of 5 K min^{-1} was used for all experiments. The results are summarised in Table 1. For Ni/SiO_2, Ni/ZrO_2 and Ni/Al_2O_3 two distinct reduction peaks were observed: a narrow peak with a maximum between 580 and 739 K, and a broad high temperature peak with a maximum between 724 and 900 K, the temperature of both peaks depending on the catalyst. In the case of the Ni/TiO_2 and Ni/CeO_2 catalysts a third reduction maximum is observed, at 769 and 1031 K, respectively. It can be clearly seen that there is a significant variation in the temperature of both the low and high temperature reduction peaks. The temperature of both the low and high temperature reduction peaks increases in the order Ni/SiO_2, Ni/TiO_2, Ni/ZrO_2, Ni/CeO_2, Ni/Al_2O_3.

Table 1
Reduction characteristics for methane partial oxidation catalysts

Catalyst	Temperature of peak maxima (K)
Ni/SiO_2	580, 732
Ni/TiO_2	588, 707, 769
Ni/ZrO_2	642, 721
Ni/CeO_2	688, 765, 1031
Ni/Al_2O_3	739, 900

3.2. Partial oxidation of methane

Partial oxidation was studied over four catalyst samples: Ni/SiO_2, Ni/Al_2O_3, Ni/TiO_2, and Ni/CeO_2. The reaction was followed using TPRS in the temperature range 300–1160 K, and a CH_4/O_2 ratio of 4:1 was used. Fig. 1 shows the selectivity towards CO formation measured over the fully reduced catalysts in the temperature range 760–1160 K. With the exception of the Ni/CeO_2 catalyst the CO selectivity is found to increase with temperature for all catalysts studied. In the case of Ni/CeO_2 the CO selectivity is found to pass through a maximum at about 1080 K. Of all the catalysts studied, fully reduced Ni/SiO_2 gives the highest selectivity for CO, with a value of 0.85 at 1160 K. Table 2 shows the maximum selectivity for CO for each catalyst, along with the temperature at which this selectivity was obtained and the corresponding selectivity towards CO_2.

The methane conversion was found to increase with temperature for all the catalysts studied. At 1160 K fully reduced Ni/CeO_2 was found to be the least active with a methane conversion of 1.09 mmol g_{cat}^{-1} min^{-1}, and fully reduced Ni/SiO_2 was the most active with a methane conversion of 3.73 mmol g_{cat}^{-1} min^{-1}.

The effect of the oxidation state of the catalyst on the partial oxidation reaction was also investigated for Ni/SiO_2, Ni/TiO_2 and Ni/CeO_2. The reasoning behind these experiments was that the oxidation state of the catalyst may change during TPRS, and so although the catalyst may start in the fully reduced state, it may not remain fully reduced during the temperature-programmed experiment. In addition to studying the fully reduced Ni/SiO_2 and Ni/TiO_2 catalysts these catalysts were also investigated in a fully oxidised state, i.e. partial oxidation was performed immediately following the high temperature calcination. Ni/CeO_2 was also investigated in a partially reduced state. For this,

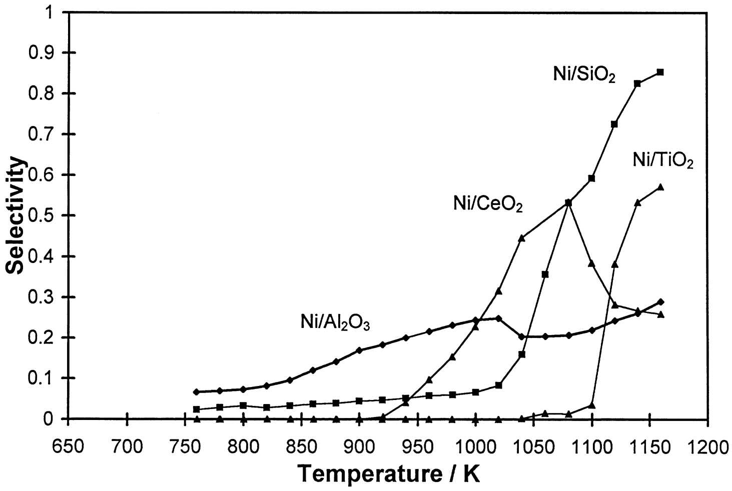

Fig. 1. Selectivity towards CO formation over supported nickel catalysts for temperature programmed reaction using a 4:1 methane/oxygen mixture.

the sample was calcined and then reduced at 728 K, which on the basis of the TPR results represented an intermediate reduction temperature which should lead to partial reduction of the nickel component and no reduction of the ceria support.

Fig. 2 shows the results obtained using fully and partially reduced Ni/CeO_2. It was found that in both cases the selectivity for CO formation passed through a maximum at about 1060 K. However, the fully reduced Ni/CeO_2 resulted in a significantly higher CO selectivity in the temperature-programmed experiment. The results for fully reduced and non-reduced Ni/TiO_2 and Ni/SiO_2 catalysts are shown in Fig. 3-Fig. 4, respectively. For these catalysts the situation is similar to that for Ni/CeO_2; in both cases the fully reduced catalysts generally give rise to a higher selectivity for CO than the oxidised samples. The difference in behaviour between the reduced and non-reduced Ni/SiO_2 catalysts is particularly marked; at temperatures below ~1000 K the selectivity towards CO is $\leq 5\%$ on the reduced Ni/SiO_2 catalyst compared to ~17% on the non-reduced catalyst, whereas at higher temperatures the selectivity for CO formation increases to a maximum of 86% at 1160 K on the initially reduced catalyst compared to a maximum CO selectivity of 39% observed on the non-reduced catalyst, i.e. a much smaller change in CO selectivity with temperature is observed for the non-reduced Ni/SiO_2 catalyst (22%) compared to the initially reduced sample where a change in selectivity of $\geq 81\%$ is observed. An interesting feature of the selectivity plots for these catalysts is the sudden change in the selectivities observed at high temperature. On fully reduced Ni/SiO_2 a sharp rise in CO

Table 2
Selectivities for CO and CO_2 for partial oxidation of methane over various catalysts

Catalyst	Maximum S_{CO}	S_{CO2}	Temperature at which maximum S_{CO} occurs (K)
Ni/SiO_2 (fully reduced)	0.854	0.139	1160
Ni/SiO_2 (unreduced)	0.390	0.520	1160
Ni/TiO_2 (fully reduced)	0.572	0.423	1160
Ni/TiO_2 (unreduced)	0.604	0.386	1160
Ni/CeO_2 (fully reduced)	0.534	0.359	1080
Ni/CeO_2 (partially reduced)	0.334	0.573	1060
Ni/Al_2O_3 (fully reduced)	0.292	0.699	1160

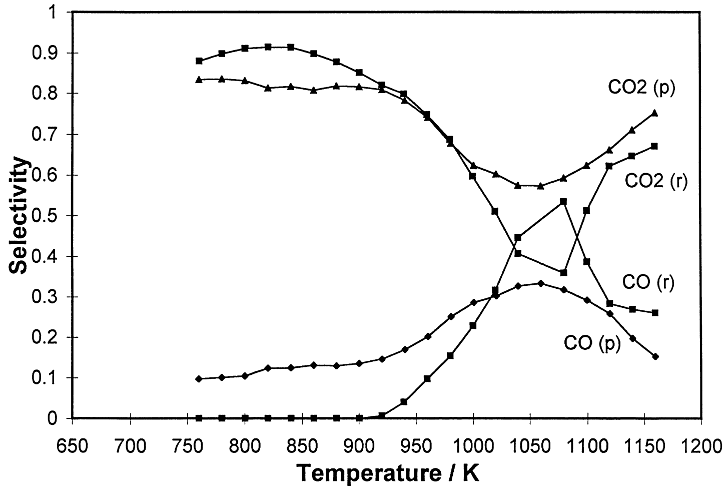

Fig. 2. Selectivities for CO and CO_2 formation over fully and partially reduced Ni/CeO_2 for TPRS using a 4:1 methane/oxygen mixture.

selectivity is observed at about 1030 K, however, this same feature is not present until 1140 K with the non-reduced Ni/SiO_2. A similar feature is observed in the case of Ni/TiO_2 where a very sudden rise in CO selectivity is observed at 1100 K for the fully reduced sample and at a slightly higher temperature of 1140 K for the non-reduced sample.

The temperatures at which methane conversion starts to occur are given in Table 3. In all cases the first product to be observed was CO_2, and this was used to measure at what temperature the reaction started. It can be seen from the table that with the notable exception of the Ni/TiO_2 catalyst the oxidation state of the catalyst has a minor effect on the temperature at which the reaction commences, however, a greater difference is seen between the catalyst samples. The reduced Ni/Al_2O_3 and Ni/TiO_2 catalysts are found to be active at the lowest temperatures (589 and

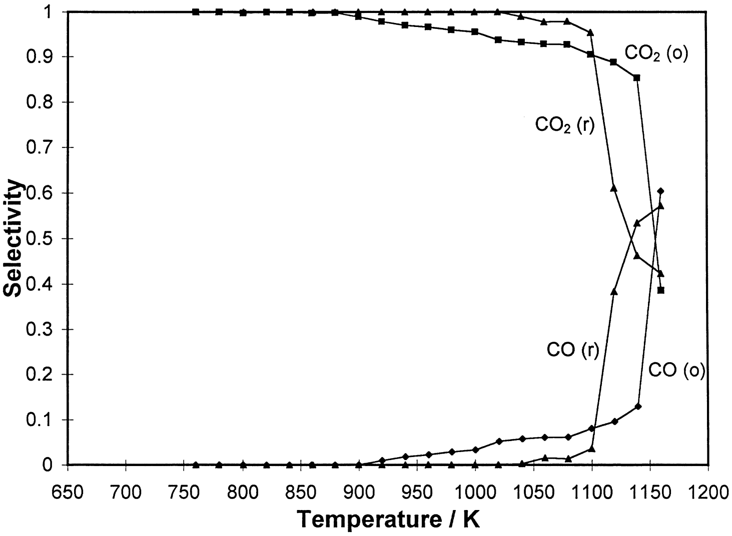

Fig. 3. Selectivities for CO and CO_2 formation over fully reduced and unreduced Ni/TiO_2 for TPRS using a 4:1 methane/oxygen mixture.

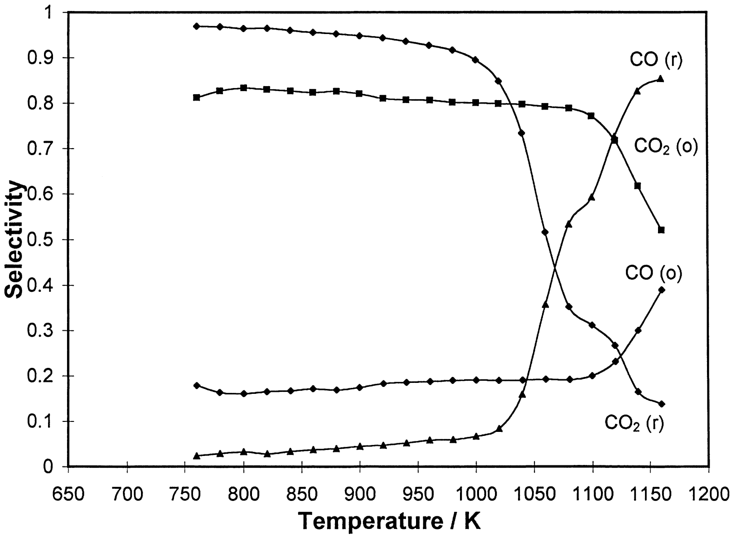

Fig. 4. Selectivities for CO and CO_2 formation over fully reduced and unreduced Ni/SiO_2 for TPRS using a 4:1 methane/oxygen mixture.

Table 3
Temperature of onset of reaction over various methane partial oxidation catalysts

Catalyst	Onset of methane conversion (K)
Ni/SiO_2 (fully reduced)	647
Ni/SiO_2 (unreduced)	657
Ni/TiO_2 (fully reduced)	594
Ni/TiO_2 (unreduced)	712
Ni/CeO_2 (fully reduced)	645
Ni/CeO_2 (partially reduced)	627
Ni/Al_2O_3 (fully reduced)	589

594 K, respectively), while non-reduced Ni/TiO_2 shows essentially no activity below 712 K.

For all catalysts studied the selectivity towards ethylene and ethane via oxidative coupling was relatively low. It was found to be highest for the non-reduced Ni/SiO_2 catalyst where 12% selectivity towards C_2 products was observed, with 8% selectivity towards ethylene formation and 4% selectivity for ethane.

Analysis by TPO following partial oxidation at 1160 K indicated that very little carbon was formed on all catalyst samples (<1% of the methane consumed), however, it was noted that this carbon was strongly bound to the catalyst, since it could only be removed from the catalyst by oxygen at high temperature. We have recently discussed types of carbon species formed on nickel/zirconia SOFC anodes and steam-reforming catalysts in another publication [15].

4. Discussion

4.1. Reduction characteristics of supported nickel catalysts

A number of groups have recently studied supported NiO using TPR [16–19]. In general, several reduction peaks are observed in the TPR profiles. Low temperature peaks are generally attributed to the reduction of larger NiO particles which are similar in nature to pure bulk NiO, whilst the high temperature peaks are attributed to the reduction of NiO in intimate contact with the oxide support. For example, in the case of Ni/SiO_2 catalysts some SiO_4 species are formed in intimate contact with NiO [16], and the reduction of NiO associated with these species occurs at elevated temperatures. From our results we propose that the two reduction peaks observed for Ni/SiO_2, Ni/Al_2O_3 and Ni/ZrO_2 correspond to bulk NiO and NiO which has a close interaction with the support. For the titania- and ceria-supported catalysts an additional high temperature reduction peak was observed at 769 and 1031 K, respectively, which can be attributed to partial reduction of the support material. TPR studies of TiO_2 and CeO_2 confirmed that these supports could be partially reduced at these temperatures [20]. From the results it is clear that the temperatures of both reduction maxima differ markedly between the different catalysts, i.e. the reduction temperature of both bulk NiO and strongly interacting NiO is altered. The variation in the temperature of the lower temperature peak, attributed to bulk NiO reduction, can be explained by differences in the NiO particle size, whilst that in the higher temperature peak can be related to different degrees of specific interaction with the support material.

4.2. *Partial oxidation of methane*

Two possible mechanisms have been suggested for the partial oxidation of methane to syngas. The first involves the complete oxidation of methane to CO_2 and H_2O followed by reforming of methane with the H_2O and CO_2 formed during the first stage of the reaction [3,13,21,22]. The second mechanism involves first the pyrolysis of methane followed by oxidation of surface carbon to CO and desorption of H_2 [7,10]. A distinction can, therefore be, made between the two mechanisms, where on the one hand partial oxidation to syngas is a primary reaction and on the other, where total combustion of methane to CO_2 and H_2O precedes steam and dry reforming of CH_4. In our TPRS measurements it was noted that the first product to be formed on all samples was CO_2. Although it cannot be concluded from such a TPRS that CO_2 is the primary product, we have recently carried out pulsing experiments which suggest that CO_2 is indeed the primary product, and thus, the first mechanism is taking place [23].

It has been suggested previously [13] that initial complete oxidation occurs on non-reduced Ni/Al_2O_3 and reforming reactions occur on the reduced catalyst. Several other authors have also reported that it is reduced Ni which is active for methane conversion and selectivity to syngas rather than NiO [6,10], and this has been attributed to the ease of formation of surface-adsorbed oxygen species which are strongly bound to the metal. Over non-reduced catalyst the surface oxygen species are more strongly oxidising as they are more weakly bound to the NiO. However, non-reduced catalysts tend to have a lower activity as the metal oxide does not easily dissociate methane to surface carbon species. CO selectivity is dependent on the ability of the catalyst to bind oxygen, while the activity is dependent on its ability to dissociate methane, i.e. a more reduced catalyst should yield a higher selectivity towards CO and have a higher methane conversion. Our results suggest, therefore, that during temperature-programmed partial oxidation the oxidation state of the catalysts do change, hence the dramatic changes in the CO selectivity at high temperature over Ni/SiO_2 and Ni/TiO_2. The change in the degree of reduction of the catalyst could be a consequence of the reducing capability of the fuel gas. It is generally believed that the fuel gas becomes more reducing as the temperature increases, so this sudden change in the selectivities probably results from the catalyst samples being reduced (or re-reduced) in the fuel feed [13].

4.3. *Conclusions*

TPR measurements on supported nickel catalysts show that two distinct types of nickel oxide are present, bulk NiO and NiO in intimate contact with the oxide support. The temperature required to reduce the NiO is strongly influenced by the NiO particle size and the support material.

Of the catalysts studied the Ni/SiO_2 catalyst exhibited both the highest activity towards methane conversion and the highest selectivity towards CO formation (85%). Ni/TiO_2 is active for methane conversion at the lowest temperature, 594 K. For all the catalysts studied CO_2 is formed in preference to CO at lower reaction temperatures. Fully reduced nickel catalysts show higher selectivity towards partial oxidation than non-reduced nickel catalysts.

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