

Coke formation on nickel–chromium–iron alloys

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Coke formation during the steam cracking of propane has been studied on foils of nickel and of a series of nickel–chromium–iron alloys with a nickel content between 8 and 74 wt%. The experiments were carried out at 810 and 850°C in a tubular flow reactor. Coke deposition was measured on prereduced foils using a microbalance. After an initial period the rates of coke deposition on the alloy foils tend to approach a common value independent of the nickel content. On the pure nickel foils a substantially higher rate of coke formation was observed. The results can be explained in terms of the surface composition of the foils as measured by Auger electron spectroscopy.

1. Introduction

Ethylene, one of the most important petrochemical intermediates, is produced mainly by the steam cracking of various hydrocarbon feedstocks [1, 2]. The reaction is carried out in tubular reactors in fired furnaces at temperatures of about 900°C, pressures of 1.5 to 2.0 bar (0.15 to 0.20 MPa) and residence times in the range of 0.2 to 0.55 sec [3]. The weight ratio between steam and hydrocarbons in the feed varies from 0.25 to 0.4 for ethane and 0.8 to 1.0 for gas oils [3]. Like most other processes involving hydrocarbon reactions at high temperatures, steam cracking suffers from the disadvantage of coke formation. Coke deposition occurs in the reactor tubes [4] and in the subsequent heat exchangers [5]. As a result of the coke deposits the heat transfer is reduced and a higher tube wall temperature is necessary in order to maintain a constant gas temperature. The reactor tubes are subjected to metal temperatures as high as 1100°C in order to maintain a gas temperature of about 900°C [6].

During decoking the coke deposits are burned out with steam–air mixtures. Decoking is usually carried out at temperatures of about 700°C [7]. The cyclic operation means that the tube material is subjected to both carburization and oxidation conditions.

As a consequence of the service conditions used in steam cracking, the selection of proper reactor materials is very important [8, 9]. HK-40 a 25Cr–20Ni steel with an average carbon content of 0.40% which has been used extensively in steam cracking [8]. However, the trend in industrial operation has been

towards high-severity operations, that is higher temperatures and shorter residence times [10]. The HK-40 steel is therefore being replaced by alloys with higher contents of nickel [11].

Although the major reactions in steam cracking occur in the gas phase, surface reactions can also be very important. It has been shown that the surface can play an important role in the formation of coke deposits [12–14]. Different metals give different rates of coke formation and nickel is known to be a good catalyst for coke formation [15–16].

The present work was initiated in order to study the relationship between an increasing amount of nickel in the steel and the rate of coke formation on the steel surface during steam cracking operations.

2. Experimental procedure

Coke deposition was studied on nickel and on different Ni–Cr–Fe alloys in a tubular flow reactor. The reactor was made of stainless steel (Uddeholm Stainless 24, 18-2689) with a quartz tube (i.d. = 14.8 mm) as an inside liner. The length of the reactor tube in the heated part of the furnace was 37 cm with a constant-temperature zone of about 15 cm.

Coke formation was measured on foils hanging from one arm of a microbalance (C.I. Electronics, Mark 2B) in such a way that the foils are in the constant-temperature zone of the reactor. The foils were all cut from larger foils to a dimension of approximately 8 mm × 32 mm. The foils were supplied by Goodfellow Metals Ltd. The compositions and thicknesses of the different foils are shown in Table I.

TABLE I Composition of foil materials*

Run	Material	Composition	Foil thickness (mm)
Ni 100		99.5 Ni	0.125
Ni 74	Inconel X	74 Ni–15 Cr–7 Fe–Ti–Al–Nb	0.20
Ni 72	Inconel 600	72 Ni–16 Cr–8 Fe	0.20
Ni 53	Inconel 718	53 Ni–19 Cr–19 Fe–Nb–Mo–Ti	0.10
Ni 20	AISI 310	20 Ni–25 Cr–Fe	0.10
Ni 8	AISI 302	8 Ni–18 Cr–Fe	0.10

* Foils supplied by Goodfellow Metals Ltd.

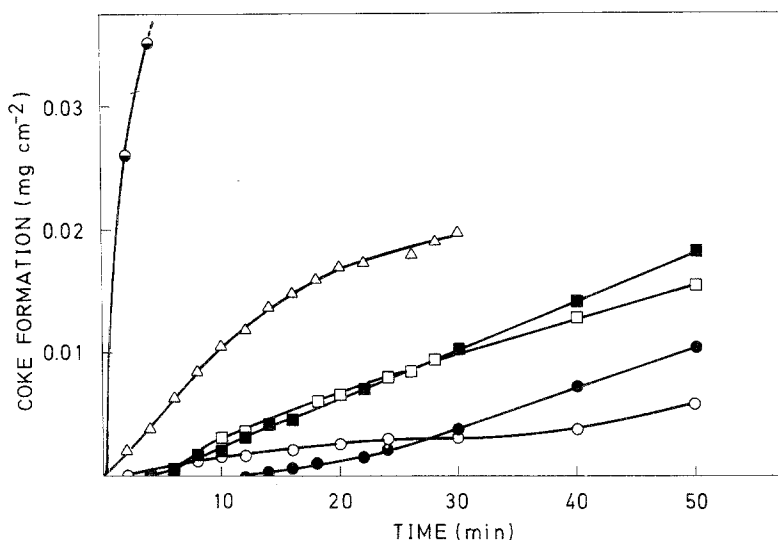


Figure 1 Coke formation on nickel and on different Ni-Fe-Cr alloys in the steam cracking of propane at 810°C. The compositions of the alloys are given in Table I. (●) Ni 100-1, (△) Ni 72-1, (■) Ni 20-1, (□) Ni 74-1, (●) Ni 8-1, (○) Ni 53-1.

The coking experiments were all carried out with propane as the feed gas and with steam and nitrogen as diluents. Steam was fed to the reactor by evaporating water into a stream of nitrogen. A stream of nitrogen was always maintained through the microbalance in order to protect the balance head.

The effluent gas from the reactor was quenched and the flow rate measured with a simple soap flow-meter. A complete analysis of the product gas was accomplished using two on-line gas chromatographs. Details of the experimental apparatus with the analytical system are described elsewhere [17]. The weight increase of the foils was measured continuously during each run, whereas the product-gas analysis was carried out 10 min after the start of a run.

After removal from the reactor, the surface of the foils could be examined by Auger electron spectroscopy (AES). The AES studies were carried out using a Varian automated Auger microprobe.

The following experimental procedure was normally applied. A fresh foil was mounted and the reactor heated to 810°C in a stream of nitrogen. Prior to use the foils had been prerduced for 18 h at 735°C. The foil was then reduced at 810°C for 1 h using a mixture of 0.144 l min⁻¹ hydrogen and 0.144 l min⁻¹ nitrogen. After the reduction, hydrogen was purged from the system and the reactor with the foil was

either allowed to cool in a stream of nitrogen and the foil removed for surface examination or a mixture of 0.13 l min⁻¹ propane, 0.11 g min⁻¹ steam and 0.19 l min⁻¹ nitrogen was fed to the reactor.

Coking experiments were also performed at 850°C. These runs followed immediately after the runs at 810°C. Only nitrogen was fed to the reactor during heating from 810 to 850°C. The foils were exposed to the coking mixture for 50 min during each run.

3. Results and discussion

Coke deposition on the different foils was studied using the given experimental procedure. With the nickel foil and the foil containing 53% Ni two runs were performed at 810°C before the run at 850°C (Experiments Ni 100-3 and Ni 53-3 in Fig. 3 below).

In Table II the conversion and the product gas composition are given for Run Ni 74 (Table I). Since the surface area of the foil is very small compared to that of the reactor surface, the foil has no measurable effect on the product gas composition or on the conversion. Carbon oxides were not detected in the exit gas from the quartz reactor, which is in accordance with other investigations [18].

As expected, the rate of coke deposition on the nickel foil is substantially higher than on the Cr-Ni-Fe alloys (Figs 1 to 3). Although the largest differences

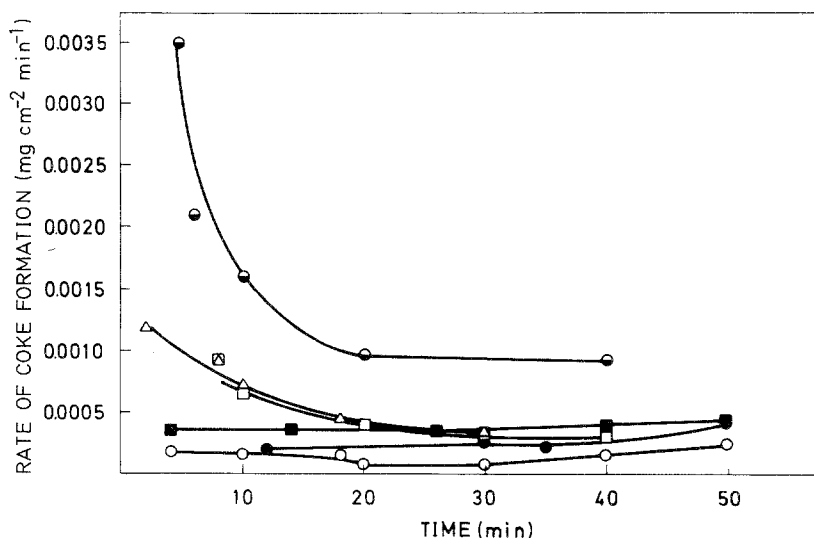


Figure 2 Rate of coke formation on nickel and on different Ni-Fe-Cr alloys in the steam cracking of propane at 810°C. The compositions of the alloys are given in Table I. (●) Ni 100-1, (△) Ni 72-1, (■) Ni 20-1, (□) Ni 74-1, (●) Ni 8-1, (○) Ni 53-1.

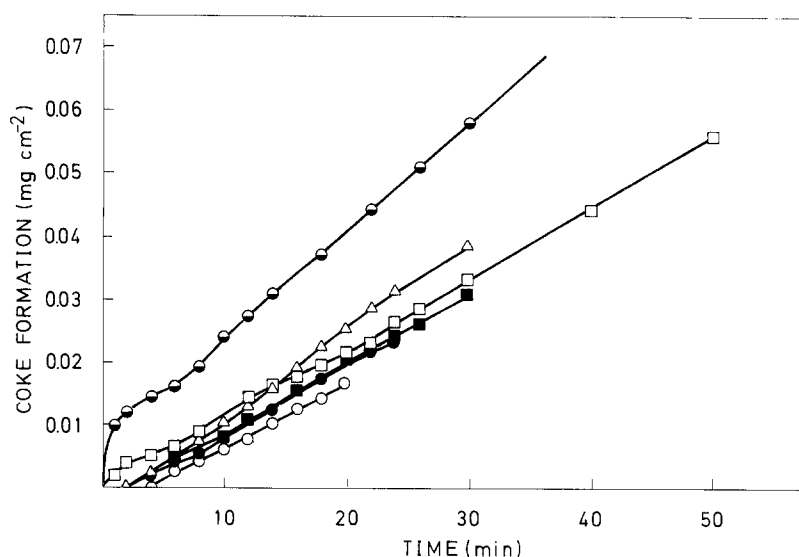


Figure 3 Coke formation on nickel and different Ni-Fe-Cr alloys in the steam cracking of propane at 850°C. The alloy compositions are given in Table I. The foils were exposed to the steam-propane-nitrogen mixture at 810°C for 50 min (2 × 50 min for runs Ni 100 and Ni 53) prior to the runs at 850°C. (●) Ni 100-3, (△) Ni 72-2, (■) Ni 20-2, (□) Ni 74-2, (●) Ni 8-2, (○) Ni 53-3.

are observed initially, the rate of coke deposition even after 50 min on pure nickel at 810°C is more than twice the value for the Cr-Ni-Fe alloys (Fig. 2).

As shown in Fig. 2, the difference in the rate of coke deposition between the various alloys is remarkably small. We observed a higher initial rate on the foils with 72% and 74% nickel (Runs Ni 72 and Ni 74), but the rates appear to approach a common value.

The lowest rate of coke deposition is observed on Inconel 718 containing 53% Ni (Fig. 2).

No induction period could be observed at 810°C nor at 850°C with the nickel foil (Figs 1 and 3). On the other foils the coke deposition showed an induction period except for the foil containing 72% Ni (Ni 72-1) at 810°C and the foil containing 74% Ni (Ni 74-2) at 850°C. It is experimentally very difficult to record small weight changes at the start of a run, but the evidence for an induction period is strong. Induction periods were also observed by Nishiyama and Tamai [19] for coke deposition during the pyrolysis of benzene in hydrogen on various steels, but not on nickel.

The rate of coke formation can be explained in terms of the surface composition. The surfaces of the foils after pretreatment with hydrogen were examined by AES. The differentiated electron energy spectrum of the nickel foil and the foils containing 72 and 53% nickel are shown in Figs 4, 5 and 6. The Auger electron escape depth is of the order of 0.5 to 2.0 nm and the detection limit is about 0.1 at % [20].

The examination of the AES spectra is concentrated on iron, nickel and chromium. Iron and nickel are known to be better catalysts for coke formation than chromium [1]. Previous investigations regarding coke formation on preoxidised steel surfaces have also emphasized this [21]. The coke formation was low on

the protective scale of chromium where no nickel or iron could be detected by surface analysis using AES. However, on the metal exposed by spalling of the chromium scale the coke formation was high. The same observation was also made by Jackson *et al.* [22] during the pyrolysis of propylene in hydrogen. Below 900°C the catalytic coking on alloys occurred where local failure sites in the protective chromium scale exposed a chromium-depleted substrate to the gas atmosphere.

Nickel could not be detected on the surface of any of the alloys (Figs 5 and 6). Even on the surface of the alloys containing 74 and 72% nickel, the AES spectra showed no nickel. Surface enrichment by chromium is a well-known feature of steel materials exposed to high temperature [23].

In terms of the nickel and iron contents on the surface, it is then reasonable to expect the same rate of coke deposition on the various alloys. Indeed, Fig. 2 shows that after an initial period this is almost the case.

According to the AES spectra there should be no nickel on the surface of the foils with a nickel content of 74 and 72%. However, the observed initial rates of coke formation on the surfaces of these two foils are higher than the rates on the other steel foils (Fig. 2). This result is strong evidence for the occurrence of a catalytic active material such as nickel or iron on the surface after prereluction at 810°C. Coke deposition deactivates the surface rather rapidly (Fig. 2), and after about 20 to 30 min no effect of the high content of nickel in the two alloys can be observed on the rate of coke deposition.

In contradiction to the present results, Suzuki *et al.* [24] have found that coke deposition increases monotonically with an increase in the nickel content of the

TABLE II Conversion and product gas composition during steam cracking of propane at 810 and 850°C

Run	Temperature (°C)	Conversion (%)	Product gas composition (mol %)						
			H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ *
Ni 74-1	810	70.5	10.2	13.2	12.8	0.6	5.3	9.5	0.7
Ni 74-2	850	91.1	11.6	18.1	17.0	0.8	3.4	2.6	0.8

*C₄ consists of 1-C₄H₈, 2-C₄H₈ (*cis* and *trans*), 1-3 C₄H₆.

Figure 4 AES spectrum of a nickel foil.

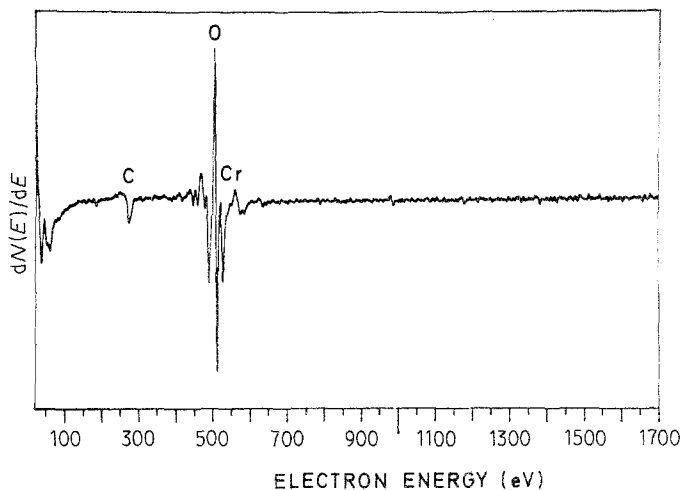
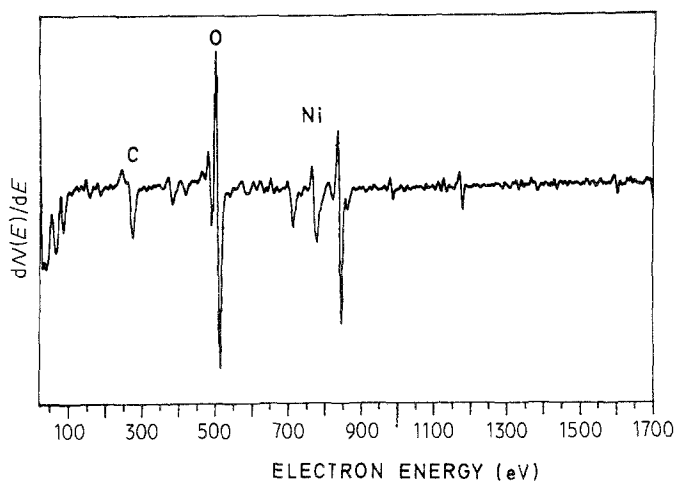


Figure 5 AES spectrum of the alloy foil with 72 wt % Ni (Ni 72, Inconel 600).

alloy. Suzuki *et al.* [24] studied the coke formation during steam cracking of ethane at 800°C. They did not use a microbalance, but measured the weight increase of the metal foils after 1 h of reaction. A reasonable explanation of this different behaviour could be found in the different pretreatments of the metal foils. Previous investigations have shown that the coking tendency is very dependent on the pretreatment [21].

From the present studies it can be concluded that coke formation on metal surfaces during the pyrolysis of propane diluted with steam at 800 to 850°C depends on the composition of the surface. Coke formation

is substantially higher on nickel than on the nickel–chromium–iron alloys. However, among the five different prerduced alloys only very small differences in coke formation are observed. The results can be explained by the formation of a protective chromium layer on the surface. Increased coke formation is observed upon destruction of this layer [21, 25].

Acknowledgement

Support for this work was provided by the Royal Norwegian Council for Scientific and Industrial Research and by Norsk Hydro A/S.

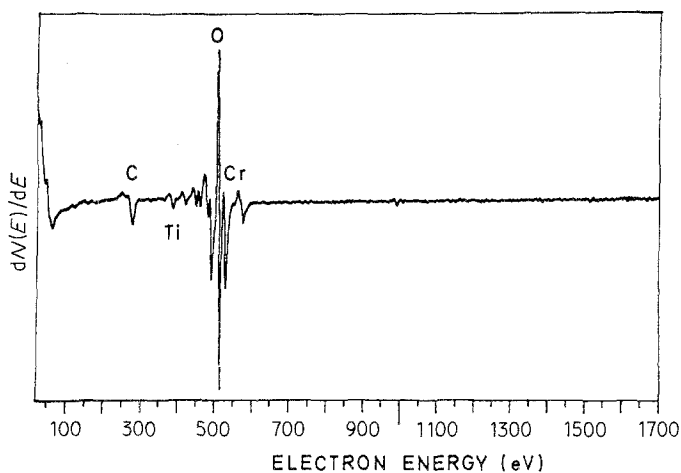


Figure 6 AES spectrum of the alloy foil with 53 wt % Ni (Ni 53, Inconel 718).

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*Received 2 March
and accepted 28 April 1987*