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Coke formation and minimisation during steam reforming reactions

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Abstract

The formation of coke during the steam reforming of light hydrocarbons results mainly from catalytic reactions. It is believed that the process is endemic to steam reforming in that the same intermediates are involved in the main reaction as are involved in coking. As a result, control of coking depends on the control of the kinetics of intermediate reactions. On an industrial scale, coking can be controlled by controlling steam/carbon ratios in the feed. It can also be minimised by ensemble size control on nickel surfaces and/or by interfering with the reactions leading to carbon. Doping with traces of sulphur or with small amounts of metals that concentrate on the nickel surface is found to reduce significantly the formation of coke. Further improvements may be possible as a result of detailed studies of support effects in the catalysis.

Keywords: Coke formation; Steam reforming

The steam reforming of light hydrocarbons has been of considerable industrial importance for many years [1–3]. The products of the reaction are controlled mainly by thermodynamics, which favour the production of methane at lower (ca. 600 K) temperatures and of hydrogen at higher (ca. 1200 K) values:

$$C_nH_{2n+2}\tfrac{1}{2}(n-1)H_2O \rightarrow \tfrac{1}{4}(3n+1)CH_4 + \tfrac{1}{4}(n-1)CO_2 \qquad (1)$$

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \qquad (2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

The greater availability of natural gas has led to considerable interest in the steam reforming of methane, a reaction which is overall endothermic:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \quad -\Delta H^0_{298} = -206\,\text{kJ/mol}. \qquad (4)$$

Supported nickel is used industrially to catalyse the reaction, since it is more cost effective than more active catalysts [1,2].

Recent attention has also been focused on carbon dioxide reforming of methane [4]:

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2, \quad -\Delta H^0_{247} = -247\,\text{kJ/mol}. \qquad (5)$$

It is questionable whether this reaction could have a significant effect on greenhouse gas emissions [4] but the reaction does provide a means of adjusting the CO/H_2 ratios in synthesis gas to values preferred for further processing.

The high temperatures associated with steam reforming to produce hydrogen also favour the formation of carbon. Four reactions may be involved [5,6]:

$$2CO \rightleftharpoons C + CO_2 \qquad (6)$$

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$$CH_4 \rightleftharpoons C + 2H_2 \quad (7)$$

$$CO + H_2 \rightleftharpoons C + H_2O \quad (8)$$

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2 \quad (9)$$

Reactions (6)–(8) are reversible, and may also form the basis of a means to remove carbon by gasification. Some idea of the importance of the reactions may be obtained from thermodynamic data, bearing in mind that carbon on catalysts behaves somewhat differently from graphite [3,4]. Using uncorrected or corrected data, it is possible to estimate minimum steam/carbon or carbon dioxide/carbon ratios to avoid coke formation during reforming [4,7]. Industrial operating conditions are adjusted to avoid coking on the basis of such calculations.

If coke is formed, it may originate from several sources [8,9]. Because of the high temperatures of reaction, coking may result from gas phase reactions leading to carbonaceous intermediates which condense on a surface [9]. The reactions involve free radical polymerisations and the addition of a diluent such as steam reduces their importance. Nonetheless, gas phase coke can accumulate on the catalyst, particularly with heavier hydrocarbon feedstocks [10].

The bulk of coke formation occurs on the catalyst surface, and the process is fairly well understood [5,6]. Hydrocarbons dissociate on the nickel surface to produce highly reactive carbon species (C_α) which are probably atomic carbon [11,12]. Most of the C_α are gasified but some are converted to less active C_β (Fig. 1), probably by polymerisation and rearrangement of C_α [11,12]. The carbon may be gasified, may encapsulate the surface or may dissolve in the nickel crystallite. The dissolved carbon diffuses through the nickel to nucleate and precipitate at the rear of the crystallite. This continuing process leads to the formation of a carbon whisker, which lifts the nickel crystallite from the catalyst surface, and eventually results in fragmentation of the catalyst.

This is one of the few cases where coke formation does not result in catalyst deactivation, apart from the small amount of encapsulation originating from gas phase carbon or traces of C_β. Nonetheless, the formation of carbon whiskers can lead to build up of pressure in the catalyst bed as a result of catalyst fragmentation and coking. Such pressure increases lead to the necessity of catalyst replacement.

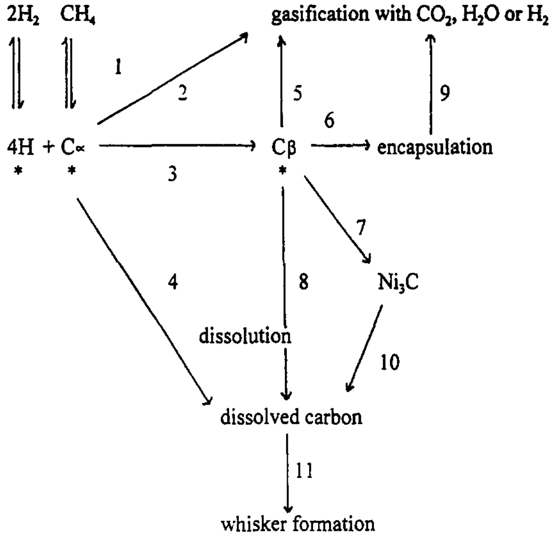

Fig. 1. The proposed mechanism of steam reforming.

It is clear that the possibility of coke formation is inherent to the steam reforming process. At least with respect to catalytic coke formation, the evidence is that the same intermediate (C_α) is involved, the extent of coking being dictated by the kinetics of the various reactions of C_α and C_β. Coke formation from reactions occurring mainly in the gas phase can occur, but catalyst deactivation by these routes is slow unless the feedstock is particularly prone to coke formation. Avoidance of coking thus demands maximal rates of gasification of coke and minimisation of one or more of the processes leading to catalytic coke.

Strategies for coke minimisation:

(1) *Coking limits.* Reactions (6)–(8) are reversible, and it is possible to calculate limits based on the ratio of carbon in the feedstock to steam or carbon dioxide beyond which carbon will not be formed [4,7]. This provides a very useful guide to desired operating conditions, but the penalties associated with the economics of superheating reagents are very real. As a result, there is continuing pressure to work at high carbon/steam ratios.

The situation can be worse when dealing with heavier feedstocks [10]. The first problem arises with traces of sulphur that may be present in the feed. When the level of sulphur is very low, this may be advantageous (see below). Under most circumstances, however, this leads to the formation of nickel sulphide and

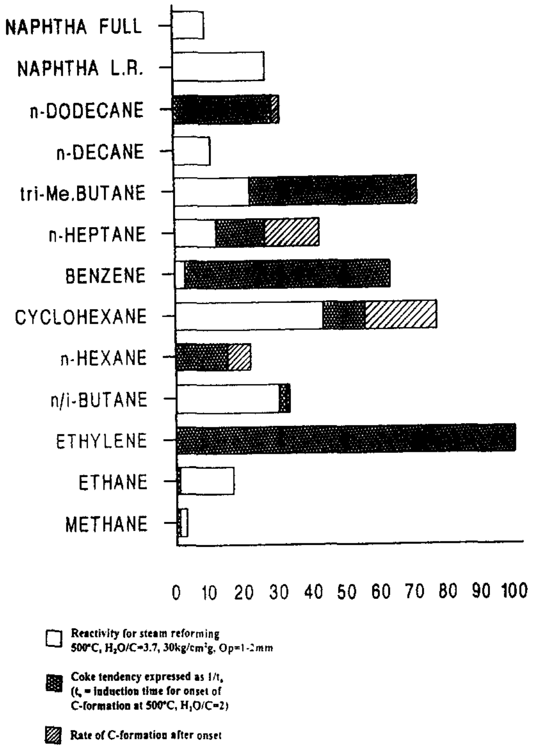

Fig. 2. The steam reforming activity and coking tendency of different hydrocarbons.

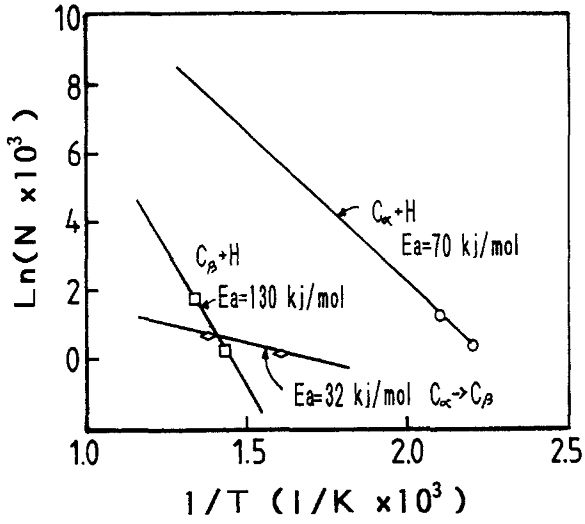

Fig. 3. The hydrogenation and inter-conversion of C_α and C_β (adapted from [12]).

to catalyst deactivation. The second problem results from the relative ratio of steam reforming to coking from various feedstocks. Rostrup-Nielsen and Tottrup [10] have reported data for a range of hydrocarbons (Fig. 2), which shows that olefins and aromatics, in particular, can pose coking problems. Both as a result of reactions in the gas phase and on the catalyst, there is a tendency for coking to increase as unsaturation, molecular weight and aromaticity in the feed increases. Steam reforming on an industrial scale of feedstocks containing up to 30 wt% aromatics has been reported [10], but such feedstocks are not desired.

Even when the ratio of steam/carbon in the feedstock is adjusted to favour gasification, the kinetics of the process may be slow. A study of the gasification of carbon deposited on catalysts by steam, carbon dioxide and hydrogen has been carried out [13] and the rates of reaction are slow. However, this study was concerned, almost certainly, with the gasification of C_β, which is known to react much more slowly with alternative gasifying agents than C_α. If polymerisation/rearrangement of C_α can be minimised, then gasification will predominate (Fig. 3). If not, the formation of C_β will result in slower gasification. In industrial operations, gasification is accelerated by the use of alkali or alkali containing supports. Magnesia- [1] and potassia- [2] based materials are mainly used, although other promoters have been developed [14]. The critical factor seems to be the affinity of the support for water [15].

(2) *The use of alternative catalysts.* Although widely used industrially, nickel is not the most effective catalyst for steam reforming. Both ruthenium and rhodium are more effective catalysts [1,2,4] on which carbon formation appears to occur via a different mechanism [4,16]. The major coking problem with nickel arises because of the formation, diffusion and dissolution of carbon in the metal [5,6]. Neither ruthenium nor rhodium dissolve carbon to the same extent and, as a result, carbon formation is less in these systems.

Despite this attraction, the cost and availability of precious metals is such that such catalysts are not used widely in industrial applications.

(3) *Control of surface reactions.*

(a) *By sulphur.* It has been demonstrated that minimal coking can be observed during steam reforming if traces of sulphur are added to the feed [4,17,18]. The resulting process has been developed industrially (the SPARG process) by Haldor Topsoe [7].

The scientific basis of the system has been well described [17]. Sulphur obtained from traces of hydrogen sulphide in the feed chemisorbs on the surface. At low coverages on a (1 0 0) surface, sulphur occupies a fourfold hollow site independent of coverage [19]. At higher coverages the surface involves a (2×2) structure on the (1 0 0) surface [20], which is probably best described as a nickel sulphide surface containing islands of free nickel sites.

Adsorbed sulphur will deactivate nickel but will also delineate ensembles of sites where sulphur is not adsorbed. Rostrup-Nielsen [17] suggested that the size of these ensembles was critical in allowing steam reforming with minimal formation of coke. Steam reforming was found to involve ensembles of 3–4 nickel atoms, while carbon formation required six or seven atoms [17,18].

The basis for the finding is easy to see from Fig. 1. Dissociation of methane to form C_α requires a given number of sites. If the formation of dissolved carbon occurs mainly through C_β, then polymerisation/isomerisation of C_α to C_β is required. This, in turn, requires at least twice the number of sites associated with the formation of C_α.

The critical ensemble size was found to be generated at sulphur coverages in excess of 0.7–0.8 (corresponding to H_2S/H_2 ratios of greater than about 7.5×10^{-7}). The rate of steam reforming was decreased, but carbon formation was essentially eliminated. Some amorphous carbon was laid down and it was possible – under extreme conditions – to produce carbon whiskers.

These whiskers were, however, of different appearance to normal whiskers and were christened "octopus" carbon. Interestingly, they have the same appearance as fibres produced on precious metals, where carbon dissolution in the metal is less likely.

Sulphur doped steam reforming has been developed into an industrial process [7]. There is a necessity closely to control the presence of sulphide in the feed to levels that are sufficient to create correct size ensembles but not to poison totally the surface. The benefit to be obtained make such control more than worthwhile.

(b) *By metals*. There is some uncertainty as to whether nickel carbide is an intermediate in the process of dissolving carbon in nickel. The carbides have been reported to be unstable above 573 K [21], and Ereksou et al. [22] could not find bulk carbides in a methanation catalyst after use at 773 K. On the other hand, traces of carbide have been identified in a steam reforming catalyst cooled after use at about 723 K [23] and carbides are known to be formed on cobalt and iron under similar conditions [24]. For nickel catalysis, it is believed that carbides are formed as short lived intermediates in the carbon dissolution process.

If this is the case, then dissolution of carbon into nickel could be minimised if carbide formation could be avoided. Trimm and ul-Haque [25] reasoned that the electronic structure of various multi-valent metals would be very similar to that of carbon, and that alloy formation with nickel could block the formation of the carbide and hence the dissolution of carbon. To minimise the amount of dopant needed, attention was focused on metals of the correct electronic structure and that would be expected to concentrate at the surface of the nickel.

As seen from Fig. 4, the addition of such dopants did have the desired effect. Steam reforming was reduced only by a small amount on the addition of traces of the dopant, but coke formation was significantly reduced. XPS measurements showed that the dopant was concentrated at the surface of the catalyst, but could give no information as to the possibility of formation of ensembles (see below).

The idea used to plan the experiments are logical but unproven. As a result, possible explanation of the observations in terms of other theories was attempted. The most obvious of these was that the dopant accelerated gasification of coke, but experimental measurements showed that this was not the case – at least in terms of gasification of C_β. The addition of ca. 2% of Bi was found to reduce gasification of C_β by about 50%.

An alternative explanation raises questions as to the relative importance of ensemble size control vs. interference with the formation of nickel carbide. It could be argued that the effect of sulphur is due to the formation of nickel sulphide and to the minimisation of nickel carbide formation rather than to ensemble size control. It could also be argued that dopants such as bismuth delineate ensembles on the nickel surface rather than inhibit nickel carbide formation.

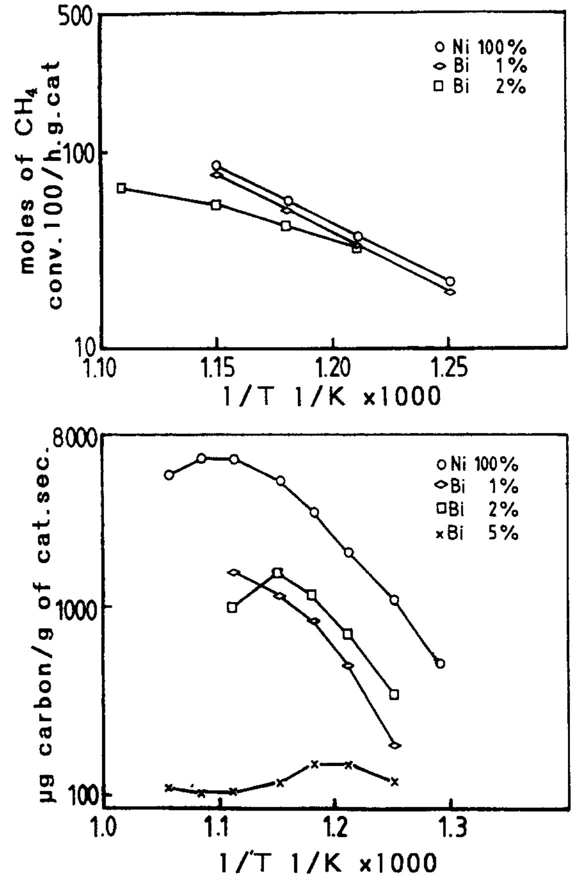

Fig. 4. Steam reforming and coking on a supported nickel catalyst in the absence and presence of Bi dopant: Steam reforming – 40 mg catalyst, total flow=300 ml min^{-1}, CH_4=27%, hydrogen=32%, steam=8%, helium=33%, temperatures as shown. Coking was studied using a microbalance – 20 mg catalyst, flow= 290 ml min^{-1}, methane=61%, hydrogen=20%, steam=7%, helium=12%.

It is certainly true that ensemble size control is important in some systems. The use of copper dopant [26], not expected to block the formation of nickel carbide, does result in a strong decrease in coking and in the formation of "octopus" type carbon at higher dopant levels. On the other hand, it could be argued that ensemble size control is not important with dopants such as Bi in that 1% addition (Fig. 4) is insufficient to delineate ensembles. However, all of the dopants that affected coke formation were able to concentrate at the surface of nickel [27]. As a result, the effective surface concentration was much higher than the bulk concentration added. However, there is no evidence either for or against the delineation of ensembles during surface concentration.

In the absence of further evidence, it seems reasonable to suggest that minimisation of coking results both from ensemble size control and from interference with nickel carbide formation.

Future trends. Steam reforming is now a mature technology where marginal gains are sought in order to make significant cost savings. It is the expensive process in any chemistry based on syngas accounting, for example, for ca. 75% of the cost of converting methane to methanol.

In the context of the reaction itself, emphasis on the chemistry of the support would seem to offer most opportunity. The Chinese were the first to recognise the advantages of adding heavier rare earth oxides to the catalyst [28], the oxides being found to slightly enhance steam reforming and dramatically enhance coke gasification. They studied the gasification of coke deposits, so the results are more relevant to C_β than C_α. Similar results were reported for ceria by Zhuang et al. [29].

The effects were suggested to arise as a result of SMSI between nickel and ceria [29]. This is not altogether surprising in view of the known advantages of the use of ceria in car exhaust catalysts, where Pt–CeO_2 and Rh–CeO_2 SMSI effects are known to have a major effect on reactivity [30]. Given that incremental improvements are desired, a more extensive study of support effects would seem desirable.

The second trend concerns the move to heavier feedstocks. Methane processing is expected to remain the major steam reforming reaction, but the availability of other feedstocks is tending towards heavier hydrocarbons.

This may mean more emphasis on partial oxidation to produce syngas. Nickel-based catalysts have been used to promote the partial oxidation of methane [31,32], but heavier hydrocarbons would seem a more obvious source of raw material. Non-catalytic initial processing would avoid considerable deactivation problems, possibly followed by steam reforming/water gas shift reactions to obtain the desired products.

The relative importance of partial oxidation vs. steam reforming would seem to be dependent on the molecular weight of the feedstock. It would be valuable to have more extensive studies of the partial oxidation processes involving such material.

It must be emphasised that this paper and this discussion have focused primarily on coking. Other forms of deactivation such as sintering or solid interactions are important with high temperature catalysis and have not been considered here. Even during decoking, deactivation by high temperature excursions is possible.

In conclusion, coking of nickel-based steam reforming catalysts is reasonably well understood. Hydrocarbons dissociate on the metal surface to produce carbon deposits which are either gasified (steam reforming) or dissolve in the nickel to produce coke. Although catalysts are not deactivated, pressure build up in the reactor requires catalyst replacement.

Avoidance of coking requires alternative catalysts which are not cost effective. Alternatively, surface doping with sulphur or other metals has been shown to control coking. It is uncertain whether this is due to ensemble size control or interference with the process of carbon dissolution.

Research on the role of catalyst supports would appear to offer most chances of improved control of coking during steam reforming.

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