# Evidence for the Participation of Surface Carbon in the Steam Reforming of Ethane over Nickel Catalysts

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*Summary* Results of experiments using isotopically labelled carbon monoxide in the steam reforming of ethane over nickel catalysts provide evidence for the participation of surface carbon species in the steam reforming of hydrocarbons.

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THE steam reforming of hydrocarbons, which can be represented by reaction (1), and the associated methanation reaction (2) and water-gas shift reaction (3) are used commercially to produce hydrogen or hydrogen–carbon mon-

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

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (2)$$

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

oxide mixtures (high-temperature processes) or methane-rich gases (low-temperature process). The literature on the steam reforming reaction has been reviewed by several authors.[1–3] One of the most detailed investigations of the mechanism of the reaction is that of Rostrup-Nielsen,[2,4] who proposed that the rate-determining steps are the breakdown of $C_2H_2$ species to $CH_x$ species and the reaction of the latter with surface oxygen species to give CO and $H_2$. One of the present authors has argued previously that a mechanism involving oxygenated surface species was possible.[1] We now have evidence for a third mechanism involving dissociation of the hydrocarbon to surface carbon atoms and subsequent reaction of these with oxygen and hydrogen to give CO, $CO_2$, and $CH_4$.[5,6] The aim of this note is to present results obtained using isotopically labelled carbon monoxide which support this suggestion.

The experiments were performed in a low-pressure constant-volume reaction system which has been described elsewhere.[7] The reaction vessel is attached *via* a capillary leak to a VG Micromass 2 mass-analyser which is used for gas analysis. The experiments were carried out using a coprecipitated Ni–$Al_2O_3$ catalyst (designated Sample 112) containing 70% Ni by weight in the reduced material, prepared according to a procedure described elsewhere.[5,6] A sample of 100 mg of the calcined material was reduced in successive doses of hydrogen at a pressure of 50 Torr (1 Torr = 133·3 N $m^{-2}$) at 873 K for a total of about 17 h. It was then subjected to a series of $CH_4$ + $H_2O$ reactions at the same temperature until the predominant product was CO, rather than $CO_2$, which is an indication that full reduction has been achieved.[7] After reduction in $H_2$ at 873 K, the Ni area of the catalyst was 8·0 $m^2$ $g^{-1}$ as determined by hydrogen chemisorption.[8] In these experiments, the area may be somewhat higher because of the higher degree of reduction obtained by the pretreatment in $CH_4$ + $H_2O$ mixtures at 873 K.[6]

Two types of experiment were carried out on the fully reduced catalyst. In the first, $^{13}C$ was deposited on the surface by the decomposition of $^{13}CO$ (96% $^{13}CO$, balance $^{12}CO$, supplied by BOC Ltd.) at a temperature of 573 K according to the Boudouard reaction (4).

$$2CO(g) \rightarrow C(s) + CO_2(g) \quad (4)$$

The extent of reaction corresponded to a fractional coverage of the nickel sites of about 1·0. A reaction of $^{12}C_2H_6$ (0·73 Torr) and $H_2O$ (2·92 Torr) was then carried out over the $^{13}C$-treated surface at 500 K. The results for the appearance of products are shown in Figure 1. Both methane and $CO_2$ are formed, the methane predominating over the $CO_2$, as described elsewhere for the reaction over a clean surface.[6] For both the methane and $CO_2$, the $^{13}C$-containing species predominated.

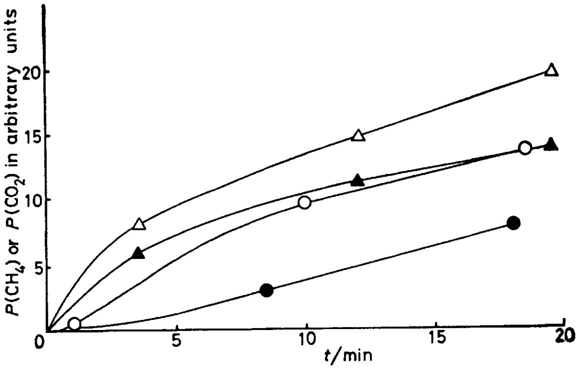

FIGURE 1. The appearance of products in the reaction of $^{12}C_2H_6$ with $H_2O$ vapour at 500 K over a coprecipitated Ni–$Al_2O_3$ catalyst on which had been deposited $^{13}C$ by the decomposition of $^{13}CO$ at 573 K. ○, $^{13}CO_2$; ●, $^{12}CO_2$; △, $^{13}CH_4$; ▲, $^{12}CH_4$.

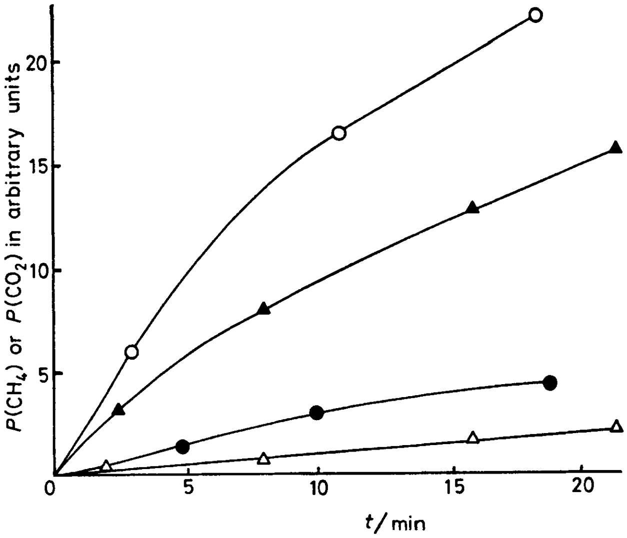

FIGURE 2. The appearance of products in a reaction of $^{12}C_2H_6$ with water vapour in the presence of $^{13}CO$ over a coprecipitated Ni–$Al_2O_3$ catalyst at 500 K. Symbols as in Figure 1.

Figure 2 shows the results of a reaction of $^{12}C_2H_6$ and $H_2O$ over a freshly reduced surface under similar conditions *to those of* Figure 1 but in which 0·73 Torr of $^{13}CO$ was added to the reaction mixture; again, only the results for the appearance of products are shown. It can be seen that $^{13}C$ appears in the $CO_2$ in a substantial proportion but that the production of $^{12}CH_4$ far exceeds that of $^{13}CH_4$.

We have shown elsewhere[6] that approximately 10% of the nickel sites of such a catalyst become covered by carbon species at the beginning of a $C_2H_6 + H_2O$ reaction and that these species behave in a very similar fashion to Boudouard carbon deposited to an equal or greater coverage. The results of Figure 1 show that Boudouard carbon participates in the reaction without changing the selectivity compared with that for the reaction over a clean surface. We therefore conclude that fully dissociated carbon species participate as intermediates in the steam reforming reaction. The results of Figure 2 show that the $^{13}C$ of $^{13}CO$ added to the $C_2H_6$ reaction mixture does not appear to any appreciable extent in the methane produced in the reaction. Hence, the methane is not formed by reaction (2) after the formation of CO or $CO_2$ but rather by the direct hydrogenation of surface carbon. The $^{13}CO$ must be excluded from the surface sites by the presence of $C_2H_6$: if this were not the case, the Boudouard reaction would occur and then results similar to those of Figure 1 would have been obtained, $^{13}CH_4$ being formed from the surface carbon. These results and conclusions are reasonable in the light of recent evidence[9] for the participation of surface carbon as an intermediate in the methanation and Fischer–Tropsch processes [the reverse of reaction (1)]. Further evidence for the participation of surface carbon in the steam reforming reaction will be presented elsewhere.[6]

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