On the Nature of Carbon in Ni/α-Al$_2$O$_3$ Catalyst Deactivated by the Methane–Steam Reforming Reaction

The mechanism of carbon formation on Ni surfaces has been studied extensively because of its importance both for coke formation on the Ni alloy reactor walls in steam cracking (pyrolysis) of naphtha or paraffinic gases in the petrochemical industry, and for catalyst deactivation in processes using supported Ni catalysts at high temperatures. Much of the earlier work has been reviewed by Rostrup-Nielsen (1) and more recently by Trimm (2). It has been proposed (3) that a diffusion of C through Ni under a concentration and temperature gradient and precipitation occurring at a dislocation are most probably involved in transportation of Ni at the surface of the growing carbon whiskers, observed by electron microscopy (4, 5). As long as the carbon whisker growth does not block the pores or encapsulate the nickel (6), it has no significant effect on the reaction rate (7). The growing whisker may, however, disintegrate (8) the catalyst, leading to increased pressure drop and other operational problems. Both carbidic and graphitic structures for the carbon on Ni have been indicated from Auger electron spectroscopic studies by Coad and Rivière (9), and quite recently by Goodman et al. (10).

In the methanation of CO (the reverse of methane–steam reforming) on Ni, McCarty, and Wise (11) have observed that two types of carbon can be formed on the Ni. Of these, the first one (α) can still be gasified, or it can become slowly transformed into a less reactive β state, which deactivates the catalyst. Pedersen et al. (12) and Gierlich et al. (13) have just reported that catalyst deactivation under industrial methanation conditions can be caused by an encapsulating carbon formation, possibly occurring from a decomposition of nickel carbide. Such a deactivation can be avoided by adjusting the process conditions to prevent the carbide formation (11).

In the context of the above studies, characterization of the carbon on Ni catalysts by other techniques is desirable. In particular, the question whether the carbon is found only on the surface of Ni, or whether it also diffuses or dissolves in Ni, needs to be answered. Information on this is sought here from temperature programmed combustion of the carbon on/in Ni and from X-ray photoelectron spectroscopy (XPS).

Commercial steam-reforming catalyst (Catalysts & Chemicals Europe, Brussels, 12% Ni on α-Al$_2$O$_3$) was used in the present studies. It had a surface area of 3.4 m^2/g and a nickel dispersion (after reduction at 750°C) of 1%. It was crushed and sieved to 0.2–0.4 mm size. After using the catalyst for kinetic studies (14) of the methane–steam reforming reaction for 250 hr at 700°C, 5 bars pressure, steam/methane ratio 5.0, and H$_2$/steam ratio 0.25, the catalyst was cooled to room temperature in a stream of pure N$_2$ and slowly and carefully exposed to air ("active catalyst"). In another case, the catalyst after the kinetic studies was allowed to deactivate by stopping addition of H$_2$ to the feed and maintaining only the flow of methane and steam over it until the catalytic activity was reduced

practically to zero. It was then cooled in N_2 and exposed to air as above ("deactivated catalyst").

Samples of the active and deactivated catalysts (0.5 g each) were taken in a quartz reactor and connected to a Wilke CO/CO_2 analyzer. A slow stream (20 ml/min.) of air was passed through the reactor while its temperature was raised linearly at 10°/min up to 720°C and thereafter kept at that temperature until combustion of the coke in the catalyst was complete. In this way both the pattern of CO_2 evolution as a function of temperature and the cumulative amount of CO_2 could be determined.

The XPS studies on the catalyst were carried out with a model 255G cylindrical double-pass analyzer of Physical Electronics Inc. Auger analysis was unsuccessful due to the poor electrical conductivity of the supported catalyst. Using Mg$K\alpha$ radiation (1254 eV) at 400 W, the XPS spectra of the deactivated catalyst were recorded in the as-received condition and after argon ion sputtering for 3, 10, 20, and 40 min. The defocused ion beam (operating conditions: 5 kV, 10 mA) has an etching rate of 1.7 nm/min on pure Fe. This value is used here for the Ni in the catalyst. For heterogeneous samples like Al_2O_3-supported Ni, the ion etching time is only indicative for the depth under the initial surface at time zero. A semiquantitative picture of the change in composition is obtained by correcting the peak heights for the photoionization cross section differences occurring for Mg$K\alpha$ as calculated by Scofield (13) and normalized by Swingle (14). During the analysis, charging effects were compensated by a flow of low-energy electrons.

The pattern of CO_2 evolution during programmed heating of the catalyst in air shows (Fig. 1) that the carbon in the active catalyst burns off completely before 500°C except for a very small portion which burns only after prolonged expo-
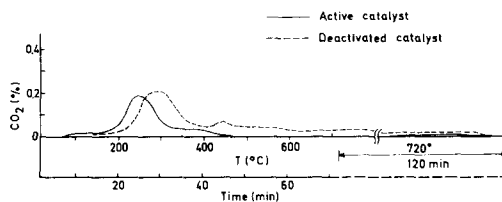

FIG. 1. Pattern of combustion of carbon from the active and deactivated Ni/α-Al$_2$O$_3$ catalysts (C content 0.023 and 0.039 wt% resp.) on programmed heating at 10°/min in air.

sure to 700°C. The carbon in the deactivated catalyst shows maximum combustion at about 50° higher than that of the active catalyst. The combustion also continues at higher temperatures and is complete only after 150 min at 720°C. From the cumulative amount of CO_2 evolved, the C content of the active and deactivated catalysts can be calculated as 0.023 and 0.039 wt%, respectively.

From the extremely slow combustion of part of the carbon in the deactivated catalyst, and the evolution of about 30% of the CO_2 only above 600°C, this part of the carbon seems to be *not on the surface* but in the bulk of the Ni crystallites, probably in a dissolved form or as nickel carbide, Ni$_3$C. This inference is supported by the XPS data given below.

The overall XPS spectrum (Fig. 2) of the catalyst shows the peaks of Ni, Al, O, and C. Peak analysis indicates that Al is present as Al_2O_3 (Al_{2p} $BE = 74.7$ eV), while O has an oxide band (531.6 eV) for Al_2O_3. Ni is identified as NiO ($Ni_{2p3/2}$ 852.3 eV). The C peak shows a shoulder formation on the lower-energy side. This peak can be deconvoluted into the major C_{1s} graphite peak ($BE = 283.5$ eV) and a C component where C_{1s} has a binding energy of 281.7 eV (Fig. 3).

After ion sputtering, Ni was detected as metallic Ni, whereas practically no change occurred for the Al and O peaks. The C peak decreased continuously with increasing sputter time. The atomic composition of the catalyst as a function of
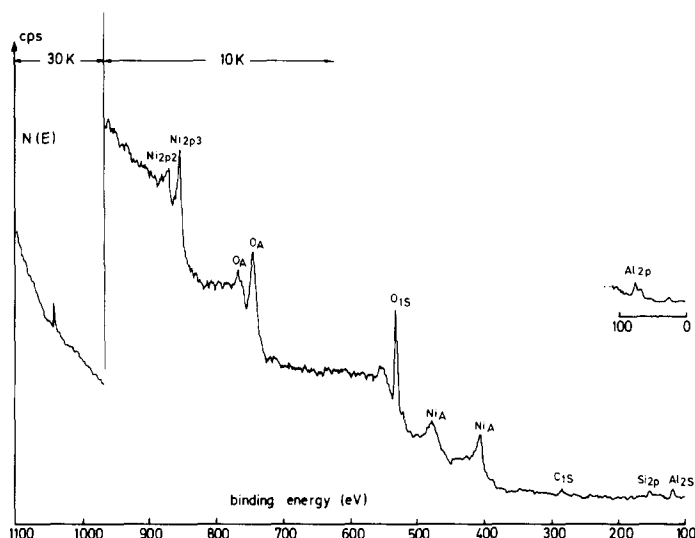
FIG. 2. Overall XPS spectrum of the deactivated catalyst in the as-received condition.

sputter time (depth from the surface) is summarized in Table 1.

The presence of partly oxidized Ni in the uppermost layers of the catalyst might be the result of atmospheric oxidation occurring while transferring the catalyst through air at ambient temperature. Reoxidation of the Ni surface by steam, in the absence of the usually necessary H_2 (see the deactivation procedure under Experimental) could also be a reason for this. Ion bombardment rapidly removes this oxide part of the Ni peak. The main C peak can be identified as typical for C in amorphous or crystalline C (no difference in XPS!) and hence is referred to hereafter as graphite. The low-energy

FIG. 3. Signal averaged C_{1s} peak of the deactivated catalyst.

shoulder of the C peak is probably caused by the presence of Ni_3C in the surface and subsurface layers of Ni, as may be inferred from the typical energy shift reported for C in the common carbides (17): for C in TaC, -2.9 eV; in TiC, -3.3 eV; in VC, -2.6 eV; in WC, -2.1 eV; ZrC, -3.7 eV. For C in

TABLE 1

XPS Analysis of Elemental Composition of the Catalyst Surface after Ion Sputtering to Different Depths[a]

Sputter time (min):	0	3	10	20	40
Approximate etching depth (nm):	0	5	17	34	68
Element (at.%)					
Ni	6.3	9.5	10.1	12.3	11.1
Al	25.7	25.1	31.3	28.5	31.6
O	54.4	52.5	47.9	52.8	54.3
C	13.6	12.8	10.7	6.4	3.0

[a] Note the continuous decrease of C content with increasing penetration from the surface, while the Ni content increases up to about 5 nm and thereafter remains practically constant. Due to shake-out and shake-up phenomena and differences in escape depth, the relative error in atomic concentrations determined by XPS could be 10–15%. To improve upon this, we have adopted the more accurate method of C. D. Wagner, Anal. Chem. 44, 1050 (1972).

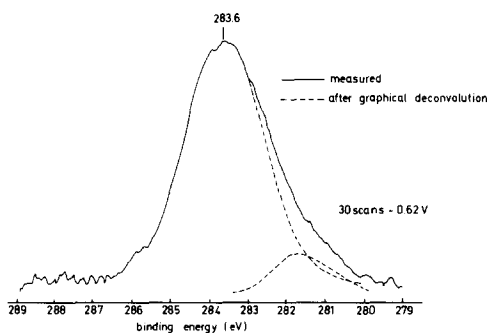$Fe_{2.25}Mn_{0.75}C$, Leroy (18) has noted a shift of -1.2 eV. Taking into consideration the correlation between binding energy and Pauling's electronegativity, the shift in binding energy for C in Ni_3C could be estimated as -1 to -1.5 eV. This is in agreement with the shift of -1.8 eV observed for the shoulder peak in Fig. 3. Furthermore the presence of C both as graphite and as Ni_3C has also been observed by Chuang (19) when surface segregation of C occurs during annealing of nickel foils. Hence one may conclude from the above results that a part of the C in the deactivated nickel catalyst is present probably as Ni_3C. The penetration of C into the Ni goes even beyond 60 nm, as shown in Table 1.

Since Ni_3C is thermodynamically metastable above 400°C, it is unlikely that it would have been initially present in the deactivated catalyst at the reaction temperature of 700°C. Instead, the carbon deposited on the catalyst (thermodynamically favored by cracking of CH_4) might have transformed from the graphitic to the carbidic form during cooling of the catalyst. The presence of C, not only on the surface but also in the subsurface layers as seen from Table 1, should facilitate this transformation. During the temperature programmed combustion, any C (carbidic or not) on the surface burns off relatively easily ($<430°C$). At higher temperatures, the graphitic C, as also the C precipitating out of the decomposing Ni_3C, can diffuse slowly to the surface and become progressively burned off. This may account for the diffusion-controlled, slow and prolonged combustion at 620–720°C (Fig. 1) until all the C in the catalyst is exhausted (see also Bernardo and Trimm (20)).

Thus, the very slow combustion of the C in the catalyst and an XPS study of the depth composition profile of the catalyst indicate that the C has diffused or dissolved into the bulk of Ni and a part of it is in a carbidic form.

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