Partial oxidation of methane to synthesis gas. Behaviour of different Ni supported catalysts

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The behaviour of Ni supported catalysts, obtained using $Ni(NO_3)_2$ and Ni-acetylacetonate as precursor compounds, is analyzed. It is observed that initial activities and selectivities are similar for both systems, but the stability differs significantly. The systems show different carbon structures and sintering rates, depending on the precursor compound employed.

Keywords: methane partial oxidation; synthesis gas; Ni catalyst; carbon deposition

1. Introduction

In general, the natural gas and its main component, methane, is converted to synthesis gas [1] via steam reforming,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \quad \Delta H = +49.2 \text{ kcal/mol}$$

This synthesis gas is a feedstock for many processes of great industrial interest, such as the production of methanol and Fischer–Tropsch synthesis [2]. In these processes, the desired H_2/CO ratio is 2, and therefore different from the one obtained by steam reforming. This ratio is, however, the one which could be obtained by partial oxidation, and alternative for the classical steam reforming process:

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2H_2, \quad \Delta H = -8.5 \text{ kcal/mol}$$

In addition to the more desirable stoichiometry, the partial oxidation reaction is slightly exothermic, while conventional steam reforming is strongly endothermic requiring large energy input (combustion furnace). A reactor based on exothermic partial oxidation reaction would be more energy efficient. Furthermore, the combustion system, in classical steam reforming, generates pollutant gases (NO_x, CO, SO_x) and CO_2, which contribute to the greenhouse effect; its elimination in a direct oxidation process would give an additional interest from the point of view of environmental protection.

High selectivities to CO and H_2 with excellent methane conversion have been reported over a number of supported transition metal catalysts, particularly Ni catalysts [3–7].

Taking into account that the operating conditions for the oxyreforming reaction are thermodynamically favorable for the sintering of Ni particles (temperature above Tamman temperature of Ni) and for carbon formation (high temperature, low O/C and H/C ratios), the analysis of the stability of the active phase is important for the development, at industrial scale, of this process.

This paper reports the use of two different precursor compounds for the preparation of alumina supported catalysts and the performance (activity, selectivity, stability) of the resulting systems in the direct oxidation of methane. One of the precursors is Ni-acetylacetonate. The use of acetylacetonates of certain transition metals as precursor compounds is a relatively new and promising route for catalyst preparation. Research performed at the French Institute of Petroleum [8,9] shows that this way of preparing supported Pd catalysts lead to solids with a high dispersion of the active phase and showing good activity and selectivity.

2. Experimental

2.1. Catalysts preparation

Two supported Ni catalysts, with 2 wt% Ni, were prepared, one using $Ni(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt) as the metal precursor compound and the other using Ni-acetylacetonate ($Ni(acac)_2$) (Aldrich). In both series, the support was α-Al_2O_3, with a specific area of 5 m^2/g, pore volume of 0.22 cm^3/g. The support was calcined in air at 873 K for 12 h, before use.

When the inorganic salt was employed, the impregnation of the support was conducted in aqueous solution, at room temperature. With the organometallic precur-

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sor, a benzenic solution at 333 K, was retained. The impregnated materials were dried in an oven at 393 K, for 2 h, and then calcined in flowing air at 1023 K, for 4 h. The catalysts prepared with inorganic or organometallic precursor were named Ni_{IN} and Ni_{OM}, respectively. The metal content was determined by atomic absorption.

2.2. Apparatus and measurements

The experimental set-up for catalytic activity measurements consisted of a tubular quartz reactor (i.d. = 0.8 cm) and an axial thermowell containing a chromel–alumel thermocouple centered in the catalyst bed.

Operating conditions with respect to total feed flow rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances. In preliminary experiments the catalyst particle size, for which intraphase transport of mass did not influence the observed rate, was determined, as can be seen in table 1. Similarly, the minimum feed flow rate, above which interphase transport resistances were minimized, was also determined following standard procedures (fig. 1). Under these conditions, the thermodynamic equilibrium conversion is near 100%.

When highly exothermic reactions, as in this case, are carried out in an experimental reactor there are two factors that must be minimized: the temperature gradient between gas phase and solid phase and hot spots that can develop within the catalyst bed. Both factors are carefully analyzed in this work. Concerning the temperature gradient between both phases, two clearly distinct mechanisms appear: heat transfer inside the solid phase and heat transfer in the gas–solid film, the latter being the one that controls, because the gas conductivity is markedly lower than the solid conductivity. Using the procedure of Froment and Bischoff [10], the maximum temperature gradient in the film was estimated in 10 K, considering methane combustion as the only reaction (heat of combustion of methane ≈ 190 kcal/mol).

Several factors affecting the presence and magnitude of hot spots were investigated: contact time, solid dilution and gas dilution. The magnitude of the hot spots is quantified by the temperature difference registered by two thermocouples, one within the catalyst bed (T_r) and one prior to the catalyst bed (T_0). Under the experimental conditions employed, the axial temperature gradient in the reactor was 4 K ($T_r - T_0$). Taking into account the preceding results, the experimental conditions were selected: atmospheric pressure, temperature range between 723 and 1123 K, feed flow rate (F) 2.9 mmol/min, with a feed composition $N_2/CH_4/O_2 = 7/2/1$. The catalyst weight was 0.050 g, and the particle size between 0.12–0.15 mm. The catalyst was diluted with pure α-Al_2O_3, with a ratio diluent/catalyst = 8/1; the length of the catalyst bed was 0.7 cm.

Table 1
Catalytic activity as a function of particle size. Operating conditions: catalyst sample Ni_{IN}; $T = 973$ K; $F = 2.9$ mmol/min; $N_2/CH_4/O_2$ ratio: 7/2/1

Particle size (mm)	CH_4 conversion (%)	CO selectivity (%)
0.833–0.351	70	86
0.248–0.147	71	88
0.120–0.104	71	85

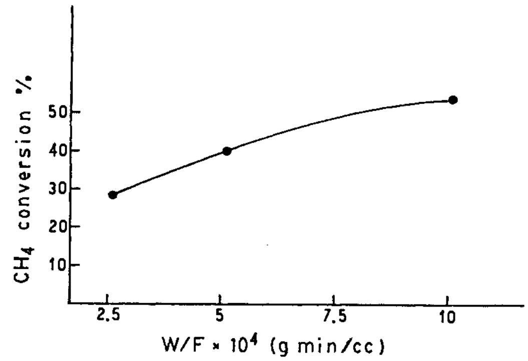

Fig. 1. Influence of contact time on the catalytic activity of Ni_{IN} sample.

The feed flow composition and the products of the reaction were analyzed with a Shimadzu GC-8A gas chromatograph, connected on line to the reactor apparatus via a gas sampling valve. Separation of H_2, O_2, CH_4 and CO occurred on a column containing 5A Molecular Sieve, whereas separation of CO_2 occurred on a column containing Porapak Q, at 313 K.

Stability tests were conducted at constant temperature (973 K), for 80 h.

The thermogravimetric analyses (TGA) were done placing the catalysts in a basket hanging from the arm of a Linseis L-72 electronic balance capable of detecting variations as small as 15 μg. The basket containing the catalyst was put in a stainless steel tube heated by an electric oven. The heating rate was 10 K min^{-1}. The temperature was measured by a chromel–alumel thermocouple located just under the basket. A N_2 sealing gas system allowed the reacting zone of the electronic balance to be isolated. The catalysts used in this study were initially in an oxidized state. The composition of the reactant feed and the reaction products was determined chromatographically.

Temperature-programmed reduction (TPR) of the catalysts was performed using a programmable furnace and the response was measured using a thermal conductivity detector connected to a recorder. The feed flow composition was $H_2/N_2 = 1/9$ and the heating rate was of 10 K min^{-1} from room temperature to 1273 K.

The reforming reaction with CO_2 was carried out in a conventional flow apparatus under the following conditions: atmospheric pressure, temperature between 823 and 1073 K, catalyst weight 0.050 g, flow rate 4.2 mmol/min, feed composition $He/CH_4/CO_2 = 10/1/2$.

Transmission electron microscopy (TEM) studies were performed using a Jeol 2010 instrument. The samples investigated by TEM were classified "R", "E" and "P", for the catalysts simply reduced (flowing H_2, 2 h, 973 K), the previously reduced catalysts left under reaction conditions (973 K) for 0.5 h and the catalysts maintained under the same reaction conditions for 80 h, respectively.

3. Results and discussion

3.1. *Effect of temperature on reaction behaviour*

Concerning the TPR results (table 2), the temperatures corresponding to the peaks of hydrogen consumption indicate that NiO is easier to reduce in the Ni_{OM} catalyst than in the Ni_{IN} one; therefore, it seems that the "precursor–support" interaction is stronger in the N_{IN} catalyst. The initial catalytic properties (activity and selectivity) are similar for both systems. The values of conversion of methane and selectivity to CO are shown in table 2 for fresh catalysts, previously reduced.

The effect of a cycle of sequential changes in reaction temperature on the conversion of CH_4 and selectivity to CO in the oxyreforming reaction has been observed by several authors in supported systems such as Rh [11] and Ni [12]. Figs. 2 and 3 show the results obtained for Ni_{IN} and Ni_{OM} catalysts in this reaction, and are in agreement with the reported behaviour. The fresh catalysts are placed in the reactor in an oxidized state. When the temperature was below approximately 1100 K, both conversion and selectivity did not increase appreciably with stepwise increasing reaction temperature, the only observed products were CO_2 and H_2O (lower part of the curves in figs. 2 and 3), and O_2 was always detected in the products of the reaction. A further increase in reaction temperature, however, resulted in an abrupt increase in conversion, with formation of CO and H_2 and completely vanishing of O_2.

When the reaction was initiated at high temperatures, approximately 1100 K, and temperature was reduced stepwise, conversion was found to be significantly higher than those observed when the experiment was conducted in an ascending temperature sequence for fresh catalysts (upper curve in figs. 2 and 3). Selectivity to CO and H_2 showed an analogous behaviour.

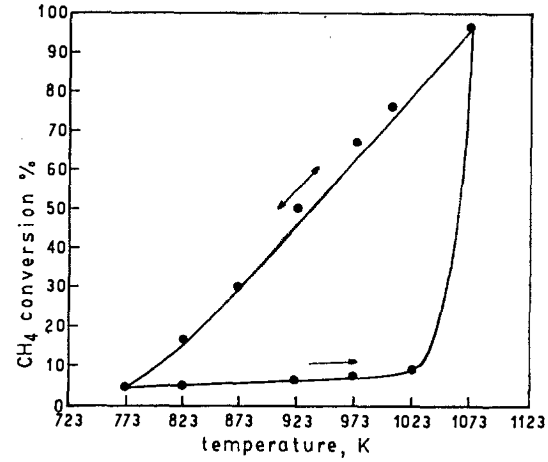

Fig. 2. Effect of reaction temperature on CH_4 conversion for Ni_{OM} catalyst. Oxyreforming reaction ($CH_4/O_2 = 2$; $F = 2.9$ mmol/min; $P = 1$ atm).

In an experiment initiated at approximately 700 K with a stepwise increment of reaction temperature up to about 1100 K and then a stepwise reduction of reaction temperature down to 770 K, the behaviour of the systems can be described by the complete cycle depicted in figs. 2 and 3. By contrast, when the experiment was initiated at 1100 K, the conversion followed only the upper part of the curves when a sequence of reduction and increment of reaction temperature was carried out, provided that temperature was not decreased under 770 K. When this was the case, only O_2, CH_4, CO_2 and H_2O were detected in the products of the reaction and the variation of conversion of CH_4 with increment of temperature followed the lower part of the curves in figs. 2 and 3, and the complete cycle could be repeated.

Taking into account our results as well as already

Table 2
Characteristics and performance of the catalysts studied at 973 K

Catalyst	Metal content (%)	TPR T_{max} (K)	Activity	
			CH_4 conv. (%)	CO sel. (%)
Ni_{IN}	2	776	71	85
Ni_{OM}	2	664	72	82

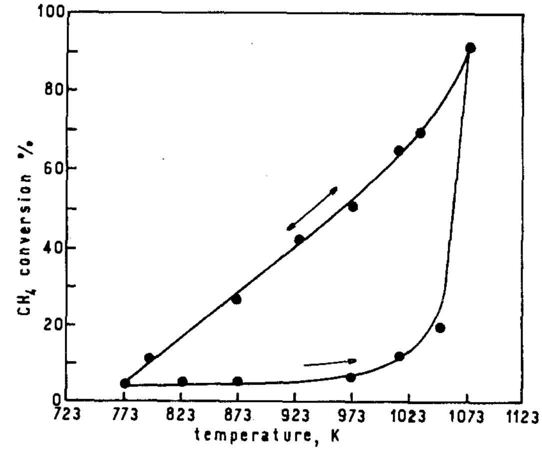

Fig. 3. Effect of reaction temperature on CH_4 conversion for Ni_{IN} catalyst. Oxyreforming reaction ($CH_4/O_2 = 2$; $F = 2.9$ mmol/min; $P = 1$ atm).

published results, it can be concluded that this phenomenon is related to alterations in the chemical state of the active phase of the catalyst, induced at high temperatures. Along with the total consumption of the oxygen present in the feed flow, high values of CH_4 conversions and selectivity to (H_2 + CO) were obtained. It is necessary to reach a temperature of around 1073 K for stoichiometric combustion of CH_4 with O_2 to be completed; then, in absence of O_2, NiO (which is not a good catalyst for CH_4 combustion) can be reduced by the remaining CH_4. The proposed mechanism for NiO reduction involves two steps: first, methane cracking reaction with H_2 generation; second, H_2 provokes NiO reduction and nickel in a zerovalent state is actually the active phase. This interpretation is in agreement with the following results:

(a) In other systems, such as Rh_2O_3/Al_2O_3, it has been observed that an abrupt increase in CH_4 conversion and selectivity to (H_2 + CO) occurred at approximately 823 K; the significant difference in the ignition temperature of the reaction is related to the difference in combustion capacity and reducibility between NiO and Rh_2O_3. Rh_2O_3 is a good combustion catalyst, as is shown in the literature [13].

(b) Thermogravimetric analysis: The catalysts used in this study were initially in an oxidized state. When the feed flow was composed of N_2 and CH_4, a weight increment of the catalyst due to deposits of surface carbon was observed from about 813 K. This weight increment was assigned to methane cracking followed by carbon deposition, for the presence of H_2 was chromatographically detected in the outlet gases. In an analogous experiment, but with a feed flow containing N_2, CH_4 and O_2, the weight increment was shifted to a higher temperature, appearing at around 1073 K. While O_2 is present, temperature must reach a value of around 1073 K to ensure that the CH_4 cracking produces the H_2 necessary for the reduction of the nickel surface. This fact would explain the abrupt increment in activity observed in the oxyreforming reaction, strengthening previous assumptions: O_2 competes with CH_4 for the cracking sites, delaying this reaction and so, reduction of the nickel surface.

(c) Reforming reaction with CO_2: in this experiment the catalysts were initially in an oxidized state. The feed flow was composed of He, CH_4 and CO_2, and the reactions taking place were:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

As in this case O_2 was not present in the feed flow, the reduction of the oxidized Ni surface was achieved at a

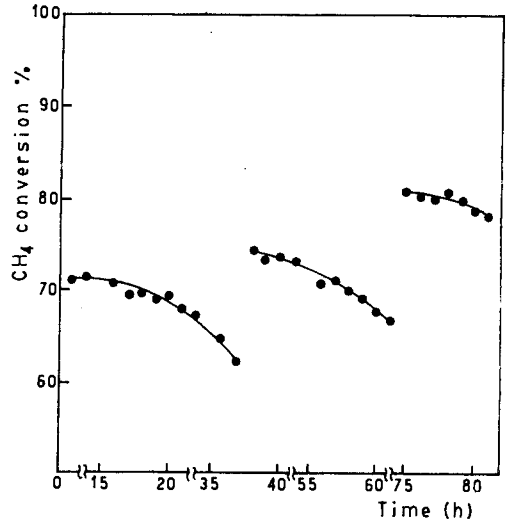

Fig. 5. CH_4 conversion as a function of time (h) for Ni_{IN} catalyst. Oxyreforming reaction (CH_4/O_2 = 2; F = 2.9 mmol/min; P = 1 atm; 973 K).

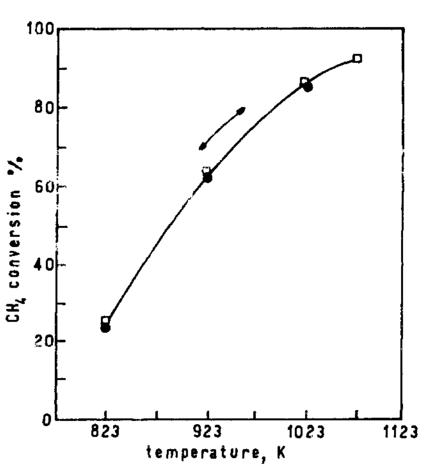

Fig. 4. Effect of reaction temperature on CH_4 conversion for Ni_{IN} catalyst. Reforming reaction with CO_2 (CH_4/CO_2 = 0.5; F = 4.2 mmol/min; P = 1 atm).

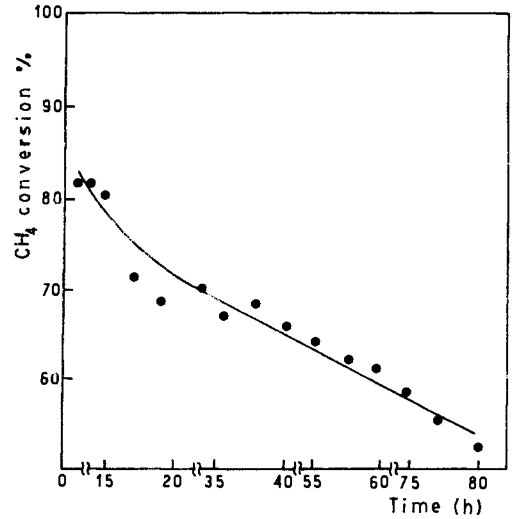

Fig. 6. CH_4 conversion as a function of time (h) for Ni_{OM} catalyst. Oxyreforming reaction (CH_4/O_2 = 2; F = 2.9 mmol/min; P = 1 atm; 973 K).

lower temperature, in agreement with the results obtained in thermogravimetric analysis when the feed flow was N_2 and CH_4. The effect of temperature reaction on CH_4 conversion is shown in fig. 4, and as can be seen, no cycle was observed because there are no changes in Ni oxidation state.

In the case of partial oxidation of methane, it was also observed that the conversion of CH_4 and the selectivity to syngas were enhanced as contact time increased. Conversely, the selectivity to CO_2 increased when the contact time was decreased. These facts suggest that the reaction follows a scheme in which CO_2 is a primary product of the reaction. This is in agreement with the following reaction pathway, which has been proposed by Dissanayake et al. [12]:

(i) consumption of O_2 with a fraction of CH_4 in a total combustion reaction;

(ii) once O_2 has been consumed, the classical steam reforming reactions take place:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

3.2. Stability tests

Catalyst samples prepared from the inorganic (Ni_{IN}) and organometallic precursors (Ni_{OM}) were tested in order to estimate their stability for the oxyreforming reaction. Figs. 5 and 6 show the evolution of the conversion of CH_4, as a function of time, for the two samples. As it can be observed, their behaviour is quite different. For the Ni_{IN} catalyst, the decrease in conversion is interrupted by sudden increments of activity, whereas for the Ni_{OM} catalyst, conversion decreases continuously.

Ni_{IN} "R" catalyst showed rounded Ni particles, with a wide particle size distribution, while Ni_{OM} "R" catalyst presented Ni particles having a similar size distri-

a

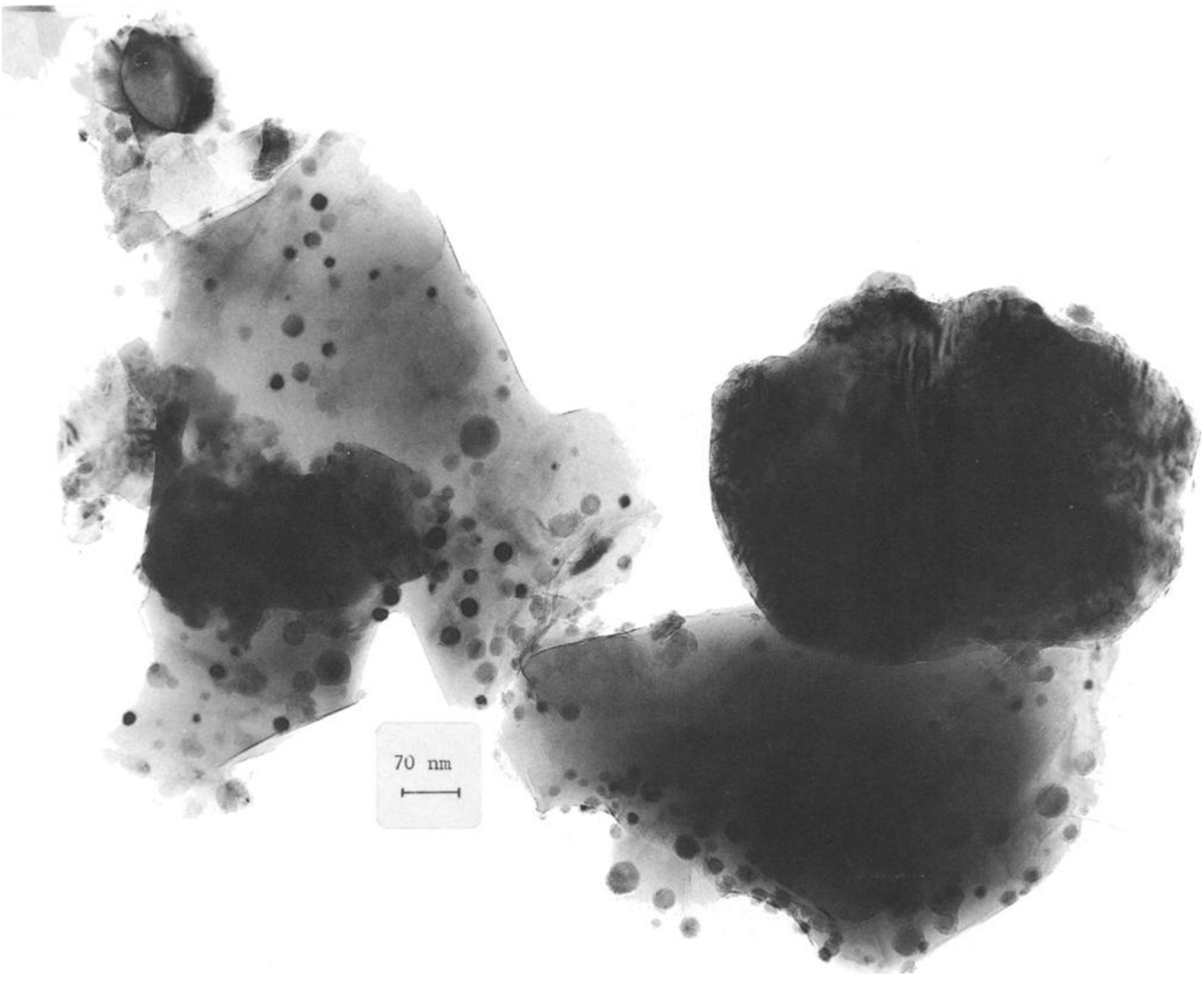

Fig. 7. Electron micrograph (TEM) illustrating the morphology of Ni particles of the reduced catalysts (flowing H_2, 2 h, 973 K). (a) Ni_{IN} "R" catalyst. (b) Ni_{OM} "R" catalyst. (Continued on next page.)

bution, but seemingly more planar, with corrugated edges (figs. 7a and 7b). This is in agreement with other authors [14] who stated that the use of acetylacetonate precursor, for supported metal catalysts, allowed obtaining a monolayer of the metallic phase on the support.

Among the samples left under reaction conditions, for 0.5 h, only Ni_{IN} "E" presented a certain coating of the Ni particle, which could be attributed to the first step of carbon deposition. The shape of the Ni particles was still quite comparable to that of the reduced catalyst.

The samples Ni_{IN} "P" and Ni_{OM} "P", obtained after 80 h on stream, differed significantly. The micrograph of Ni_{IN} "P", presented in fig. 8a, shows the presence on the catalyst of tubular carbon filaments (whisker carbon). A Ni particle, with diameter close to 15 nm, appears at one extremity of the filament. Another form of carbon, encapsulating completely some Ni particles, can also be seen in this sample.

The micrograph of Ni_{OM} "P", on the contrary, did not show carbon filaments or encapsulating carbon. As seen in fig. 8b, most of the Ni particles have strongly sintered and appeared to have lost their contact with the support.

In the light of these results, and explanation for the different behaviour displayed by the two catalysts, can be presented. As it has been previously mentioned, the Ni_{IN} catalyst has a wide distribution of particle size. Besides, the reaction is carried out under conditions that favor sintering.

The formation of two different types of carbon over Ni catalysts under conditions of steam reforming reaction, one deactivating (encapsulating carbon) and the other not (whisker carbon), has been studied extensively [1,15–17]. It has been reported that a minimum diameter of the Ni particles of about 10 nm, together with a minimum C/Ni^s ratio of the order of 8–10 carbon atoms adsorbed per superficial Ni are necessary for the forma-

b

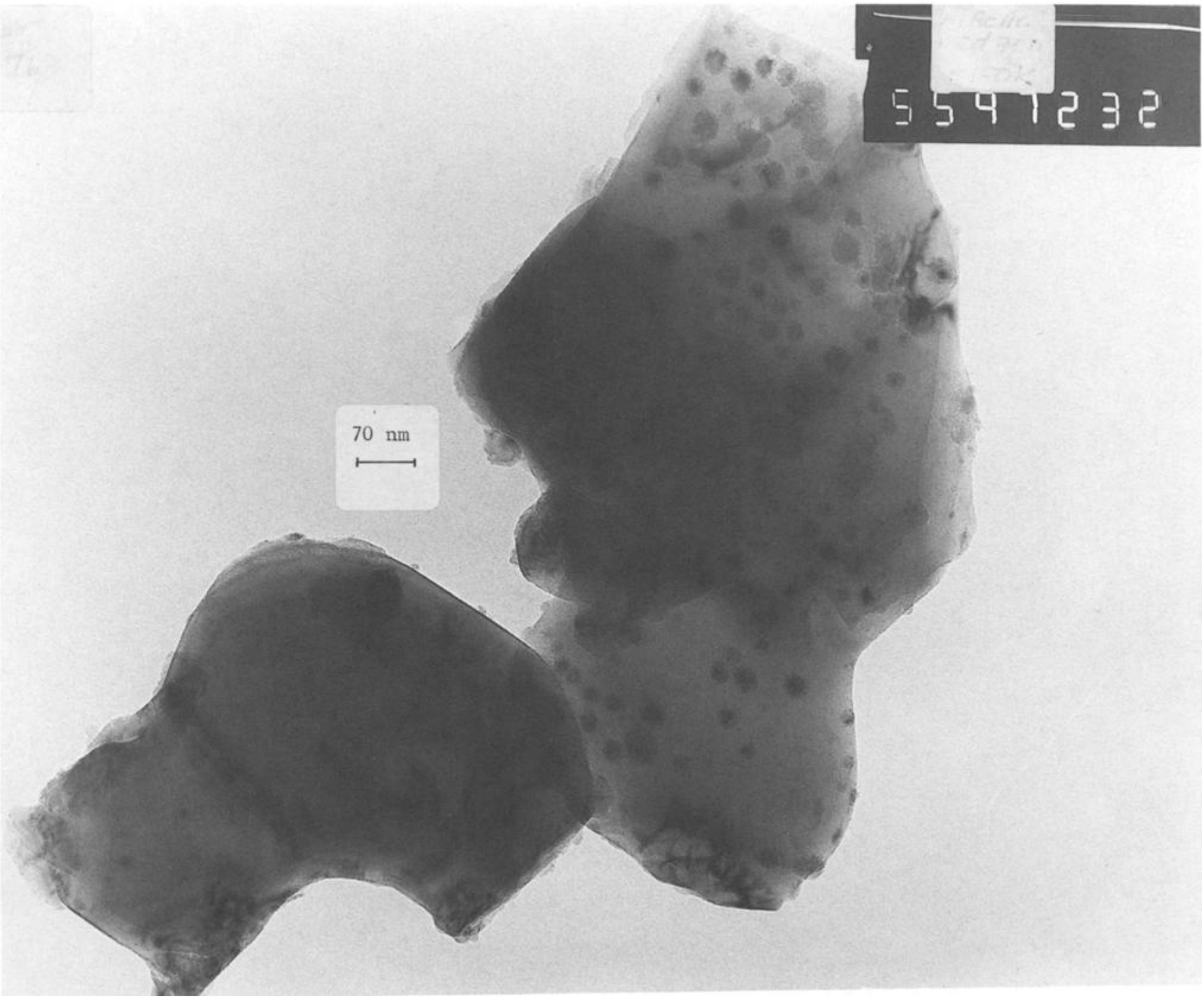

Fig. 7. (Continued.)

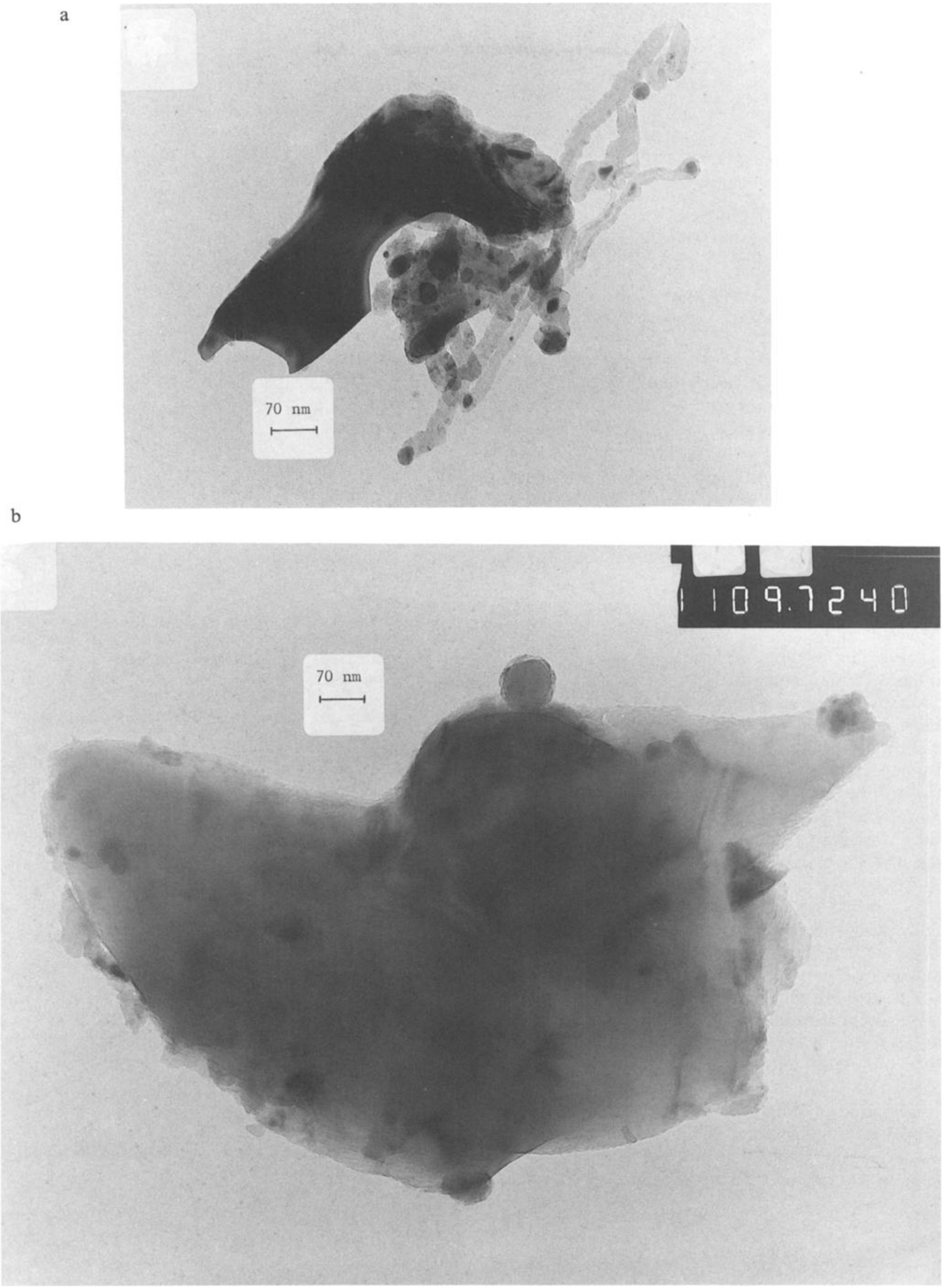

Fig. 8. Electron micrograph (TEM) illustrating the morphology of carbon deposits on Ni catalyst left under reaction conditions for 80 h (973 K). (a) Ni_{IN} "P" catalyst. (b) Ni_{OM} "P" catalyst.

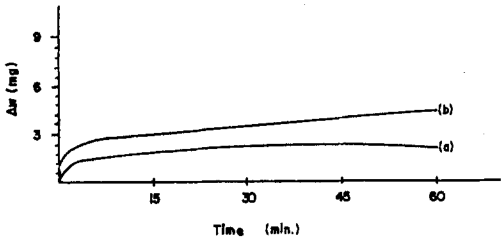

Fig. 9. Carbon content vs. time on stream (min). Feed flow composition: $N_2/CH_4/H_2 = 15/5/1$, $T = 973$ K. (a) $\mathrm{Ni_{OM}}$ catalyst. (b) $\mathrm{Ni_{IN}}$ catalyst.

tion of whisker carbon [18,19]. This process provokes some kind of reorganization and reconstruction of Ni particles at the extremity of carbon filaments. These Ni particles are again accessible to reactants and consequently, the activity of this Ni is not restrained. Nevertheless, it is necessary to avoid the formation of whiskers when working in a continuous process, because it can destroy the catalyst texture and structure.

On the other hand, small particles are not able to produce a filament, and they become easily encapsulated by the growing deactivating carbon.

The coexistence of the factors mentioned hereto seems to explain the behaviour of the $\mathrm{Ni_{IN}}$ catalyst depicted in fig. 5, for which successive periods of decrease in conversion are interrupted by sudden improvements in activity.

In the case of the samples prepared via the organometallic route, and in spite of having similar initial Ni particle size as the $\mathrm{Ni_{IN}}$ catalyst, neither precursors of carbon formation ($\mathrm{Ni_{OM}}$ "E") nor whisker carbon, at the end of the test, have been observed ($\mathrm{Ni_{OM}}$ "P"). There is an important increase in the size of Ni particles and some of them are no longer supported, leading to a continuous deactivation of the catalyst.

In order to study the behaviour of both systems ($\mathrm{Ni_{IN}}$ and $\mathrm{Ni_{OM}}$) under thermodynamically severe conditions towards carbon deposition (feed flow composition $N_2/CH_4/H_2 = 15/5/1$, 973 K), thermogravimetric studies were carried out. The curves of carbon content versus time are shown in fig. 9. It can be observed that the carbon deposition is greater for $\mathrm{Ni_{IN}}$ catalyst in agreement with TEM results, which showed an appreciable amount of carbon, principally whisker-like structures.

The need of stabilizing the active phase in Ni supported catalysts prepared using $\mathrm{Ni(acac)_2}$ as precursor, by decreasing the sintering rate and reinforcing the Ni–support interaction, is a subject that deserves deeper research. Taking into account that catalysts having the capacity of developing whisker carbon cannot be used on industrial scale, the results obtained with $\mathrm{Ni_{OM}}$ catalysts suggest that the organometallic route for preparation of supported Ni catalysts could be a field of great interest.

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