The Influence of Inert Impurities on the Catalyst Lifetime and Properties of Nanofibrous Carbon Produced by Utilization of Diluted Hydrocarbon Gases

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Abstract

Experimental studies were focused on the feasibility of utilization of hydrocarbons diluted with inert gases (such as associated oil gases) during the synthesis of nanofibrous carbon. The carbon yield and catalyst lifetime were studied regarding the initial reaction mixture parameters. Varying the composition of the initial gas mixture, it is possible to control textural characteristics of the resulting carbon product.

INTRODUCTION

Synthesis of nanofibrous (filamentous) carbon by decomposition of hydrocarbon gases in the presence of metal catalysts is becoming increasingly important at present. This material is very promising as a catalyst support [1], electrode material [2], as a support for immobilization of biologically active substances [3], as a catalyst [4] and additive to polymers [5]. Besides, nanofibrous carbon is a good adsorbent and can be used for cleaning the waste from harmful impurities [6].

The material is formed by carbon fibers ranging from 3 and 500 nm in diameter. Nanofibers have a graphite-like structure. Depending on the catalyst type and reaction conditions, the basal graphite planes may be arranged either as a coaxial cylindrical system (multilayer nanotubes), or at some angle to the fiber axis to form a system of cones put one into another, or a package. The use of heavily loaded metal catalysts allows one to produce nanofibrous materials not only as individual fibers or unstable conglomerates that can be easily dusted, but also as strong porous granules [7], formed by densely packed interlaced nanofibers. The mechanism of formation of individual nanofibers and porous granules is described elsewhere ([5, 8] and [7], respectively).

The simplicity of process accomplishment makes it possible to utilize associated oil gases as hydrocarbon feedstock. The process permits wasteless utilization of associated oil gases to produce valuable products – hydrogen and nanofibrous carbon.

The aim of present paper was to investigate the influence of inert impurities in the initial gas mixture on the following characteristics of hydrocarbon decomposition: yield of carbon, catalyst deactivation, and properties of the resulting granulated nanofibrous carbon material.

METHODS

Nanofibrous carbon materials were synthesized in the installation, providing an ideal gas mixing in the microreactor with a fluidized catalyst bed. The catalyst mass was 0.002 g. To prepare a mixture, high-purity CH_4 (not less than 99.99 %) and inert gases (Ar, He, N_2) were used. The amount of mixture fed into the re-

actor was such that the constant consumption of methane constituent was provided as in the experiments with pure methane (120 l/(h g_{cat})). The experiments were carried out at atmospheric pressure. Temperature was varied in the range of 475−600 °C. The outlet gas mixture was analyzed chromatographically during the process. The samples were examined by transmission electron microscopy (TEM) using a JEM-100CX microscope (resolution 2 Å, accelerating voltage 100 kV, spherical aberration of the object lens 2.8 nm; magnification 10 000 to 100 000).

Two types of Ni-containing catalysts were used to synthesize carbon materials. The first type was prepared by co-precipitation. The components were precipitated from aqueous solutions of Ni(NO$_3$)$_2$ · 6H$_2$O and Al(NO$_3$)$_3$ ·9H$_2$O taken in the specified ratio, with NaOH serving as a precipitating agent [9]. The second type of catalysts was prepared by sol-gel synthesis method [10]. Catalysts of this type were produced with two different dispersions of active nanoparticles. In the reduced state, average size of Ni nanoparticles was 12 or 60 nm in diameter.

The experiments were divided into two series. The aim of first series was to elucidate dependencies between the total yield of carbon product, the rate of deactivation of the first type of catalysts and parameters of the reaction medium. These experiments were conducted until complete catalyst deactivation. As soon as the process stopped, the resulting carbon was unloaded from the reactor and weighed.

The second series of experiments was devoted to studying of dependencies between average nanofiber diameter and carbon growth conditions. In these experiments, the nanofibrous carbon was synthesized during 1.5 h in the presence of the second type of catalysts, and then the samples were examined by means of TEM. The micrographs obtained were analyzed, and 450 fragments of nanofibers from every sample were measured. Results of this analysis allowed us to determine the typical diameter of nanofibers for every carbon growth condition used.

RESULTS AND DISCUSSION

Figure 1 presents the results obtained for the first series of experiments using methane/
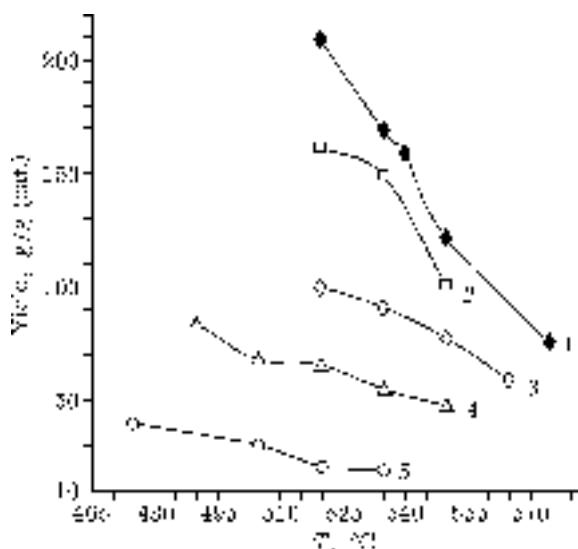

Fig. 1. The influence of argon concentration in methane on nanofibrous carbon yield, %: *1* − CH$_4$, *2* − CH$_4$ (75) + Ar (25), *3* − CH$_4$ (50) + Ar (50), *4* − CH$_4$ (25) + Ar (75), *5* − CH$_4$ (10) + Ar (90).

argon mixtures. When the inert gas is added, the total carbon yield (the yield observed after complete catalyst deactivation) decreases. Note, that carbon yield decreases with increasing the temperature at any concentration of the inert admixture. Probably, this decrease is due to a more rapid catalyst deactivation at relatively high temperatures.

Figure 2 shows the curves of methane conversion versus time at different argon concentrations in the reaction mixture. The time of complete catalyst deactivation becomes short-
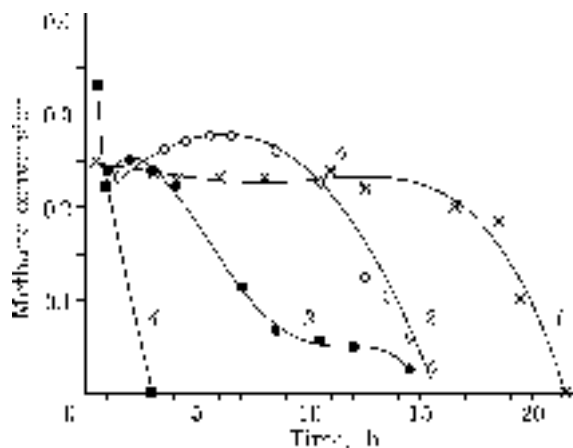

Fig. 2. Dependence of methane conversion on the time of catalyst operation at different proportions of argon in the inlet mixture. Temperature 535 °C. Initial mixture, %: *1* − CH$_4$ (100), *2* − CH$_4$ (90) + Ar (10), *3* − CH$_4$ (80) + Ar (20), *4* −CH$_4$ (10) + Ar (90).
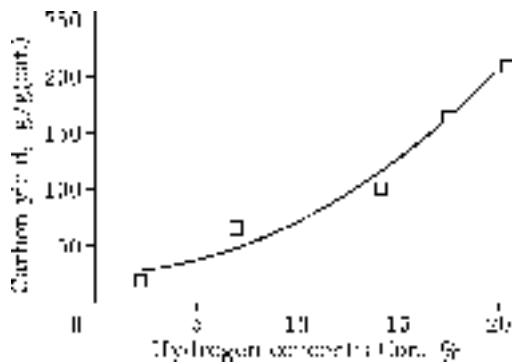
Fig. 3. The influence of hydrogen concentration in the reaction medium on nanofibrous carbon yield. Temperature 520 °C.

Fig. 4. The sample of nickel catalyst deactivated at 600 °C. 10 % CH_4 + 90 % Ar gas mixture was used as a feedstock.

er as concentration of the inert admixture increases. In particular, the catalyst is deactivated as soon as the gas mixture is fed into the reactor, when the concentration of inert gas is very high. It should be noted that the above phenomena (see Figs. 1 and 2) are independent on the nature of inert gas. For nitrogen, helium, and argon, the behavior of methane-inert gas mixtures was similar.

Analyzing the results obtained, we established that inert gas influences the catalyst deactivation and yield of the resulting carbon by changing the partial hydrogen pressure. This observation is confirmed by Fig. 3, where different concentrations of hydrogen in the reaction medium were obtained by varying inert admixtures.
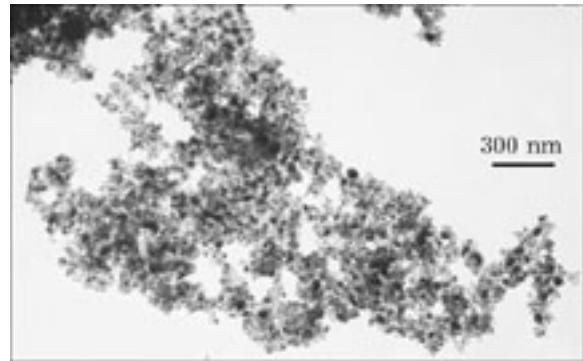
Earlier hydrogen was already reported to reduce deactivation of the catalyst and increase the carbon yield. Positive influence of the hydrogen presence was described by Chesnokov and Buyanov [11, 12], authors of the article [13, 14] and several other researchers [15, 16].

The comparison of experimental data suggests, that a decrease in the carbon yield at high concentrations of the inert gas is caused by fast catalyst deactivation due to low partial hydrogen pressure under these conditions. Figure 4 shows a micrograph of catalyst particles completely deactivated at 600 °C, when 10 % CH_4 + 90 % Ar initial reaction mixture was used.

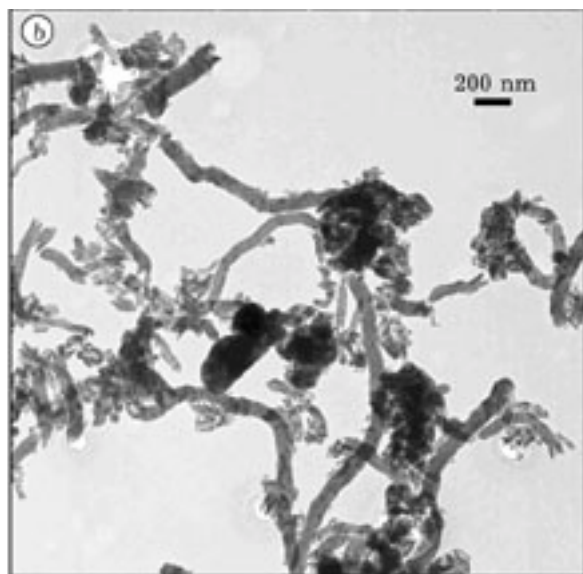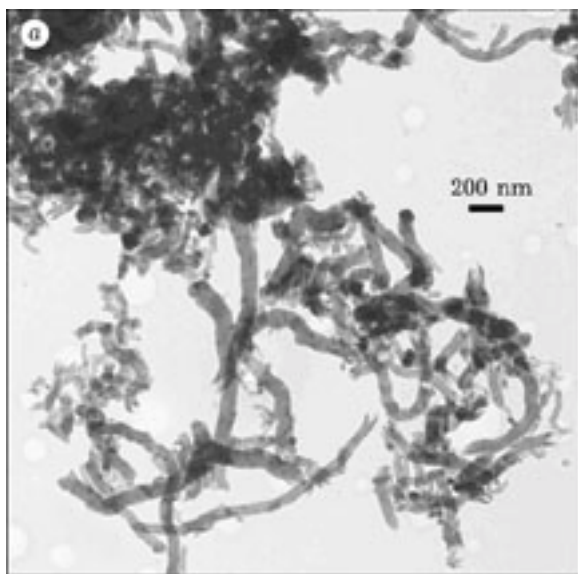The second series of experiments showed the dependence between average nanofiber

Fig. 5. Self-organization effect for carbon nanofibers obtained from 100 % CH_4 at 600 °C: a and b − initial average sizes of nickel particles are 12 and 60 nm, respectively.
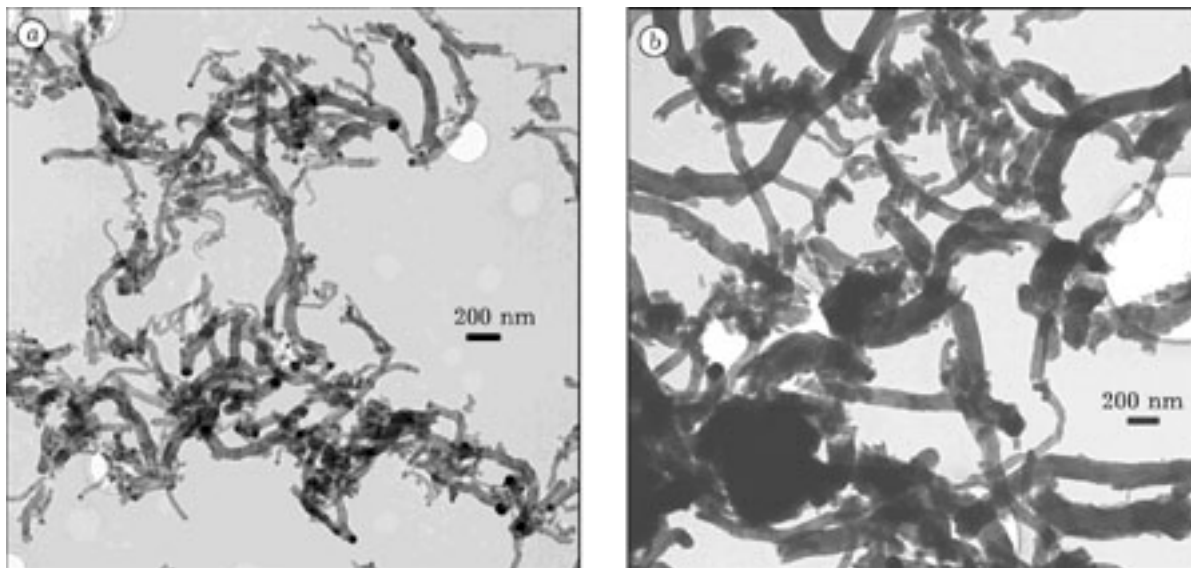
Fig. 6. Carbon nanofibers obtained from 100 % CH_4 at 500 °C: *a* and *b* − initial average sizes of nickel particles are 12 and 60 nm, respectively.

diameter and carbon growth conditions. Under some conditions, self-organization of the catalytic system takes place. Average diameter of carbon nanofibers is the same independently from initial dispersion of the active nickel nanoparticles. Self-organization of the catalyst particles is the phenomenon of changing their initial size (increase or decrease) during the process of catalytic decomposition of hydrocarbons to yield catalytic filamentous carbon.

According to the experimental data, temperature affects self-organization. As it follows

from Fig. 5, at the conditions of 100 % CH_4 initial mixture and temperature of 600 °C, the process of self-organization is finished after 1.5 h of the reaction. Average diameter of nanofibers in both samples is similar (50−70 nm) and does not depend on the initial dispersion of catalyst active component. When the initial size of particles is 12 nm, they undergo agglomeration, while, on the contrary, particles of 60 nm decrease in size. Nanofibers with the similar diameters form also on the catalysts with different initial dispersions of the active component at 550 °C using
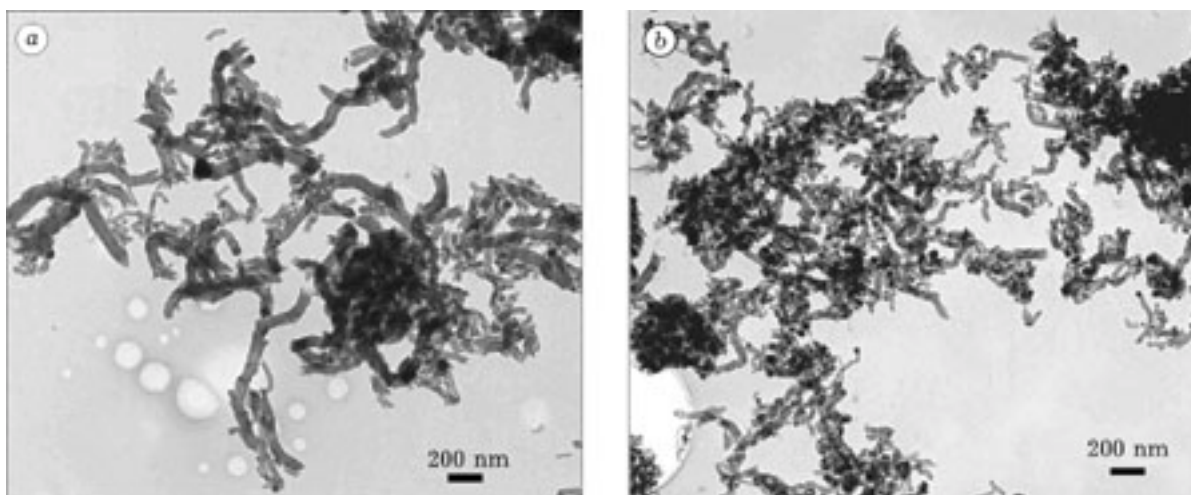

Fig. 7. Carbon nanofibers obtained at 550 °C (initial average size of nickel particles is 12 nm): *a* − 50 % CH_4 + 50 % Ar; *b* − 10 % CH_4 + 90 % Ar.

TABLE 1

The influence of temperature and argon concentration in methane on nanofibrous carbon yield, g/g_{cat}. Experiment time – 1.5 h

T, °C	Initial average size of Ni nanoparticles				
	12 nm			60 nm	
	CH_4	50 % CH_4 + 50 % Ar	10 % CH_4 + 90% Ar	CH_4	50 % CH_4 + 50 % Ar
500	8.7	10. 8	13.9	6.2	12. 7
550	17.9	20.7	13.0	11.4	7.4
600	27.4	26.0	1.3	13. 4	4.1

100 % CH_4 and at 550, 600 °C using 50 % CH_4 + 50 % Ar initial mixture. The typical diameters were in the range of about 50–60, 40–50 and 30–40 nm, respectively.

At 500 °C the effect of self-organization is not observed (Fig. 6) for all the initial mixture compositions used.

Thus, the effect of self-organization of nanoparticles of the nickel catalyst, during decomposition of hydrocarbons producing filamentary carbon, is observed for 550, 600 °C and 100 % CH_4, 50 % CH_4 + 50 % Ar initial mixtures. The experimental results comply with the data in Ref. [17], where the self-organization of catalytic system was found at 550 °C for 100 % CH_4 initial mixture. The results show, that diameter of the catalyst particles tends to an average value, which is optimal for the given experimental conditions.

The mechanism of "agglomeration and dispersion" of initial nanoparticles of the catalyst is a very interesting and important problem. At present this problem is under investigation.

It should be noted, that an increase in the concentration of inert admixture and in temperature results in the catalyst deactivation which, in turn, reduces the yield of carbon. The yields of carbon after 1.5 h of carbon nanofibers growth are shown in Table 1. For large catalyst particles (60 nm), the deactivation is especially strong.

Figure 7 shows the micrographs of carbon nanofibers grown at 550 °C, at the initial dispersion of catalyst active component equal to 12 nm. With a change of initial reaction mixture 50 % CH_4 + 50 % Ar to a mixture of 10 % CH_4 + 90 % Ar, typical diameters of nanofibers decrease from 40–50 to 20–30 nm.
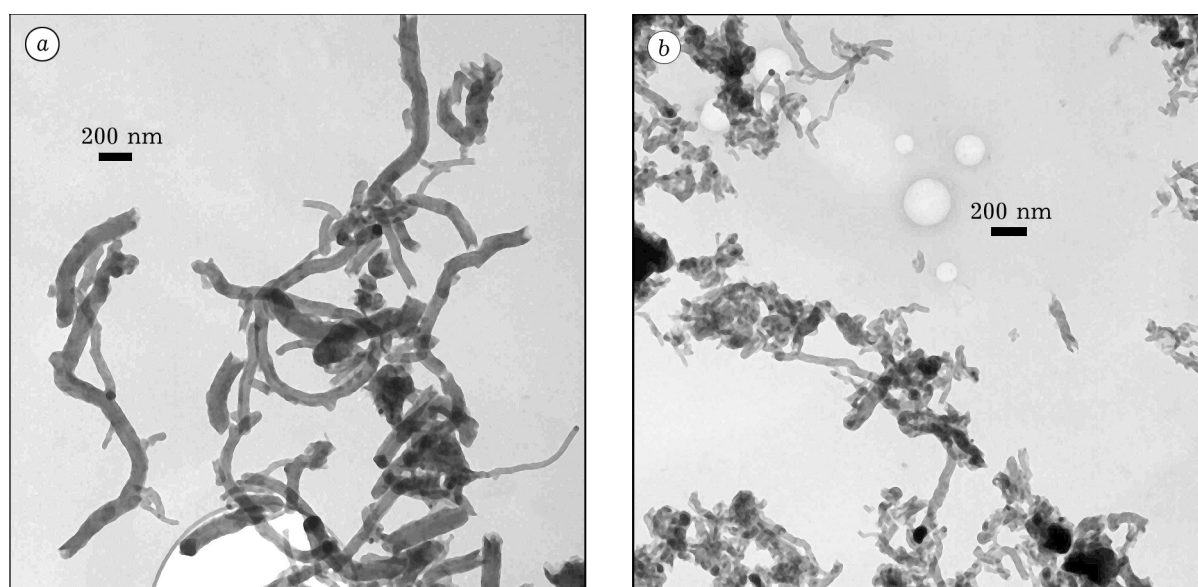

Fig. 8. Carbon nanofibers obtained from 50 % CH_4 + 50 % Ar mixture (initial average particle size is 60 nm): a and b – carbon growth temperatures are 500 and 600 °C, respectively.

A decrease in the average diameter of nanofibers with increasing temperature was observed for the sample series obtained using 50 % CH$_4$ + 50 % Ar mixture and the catalysts, in which the initial dispersion of active component was 60 nm. The diameter of nanofibers decreases from 60–80 (at 500 °C) to 30–40 nm (at 600 °C). Figure 8 illustrates this observation.

Thus, typical diameter of carbon nanofibers strongly depends on the carbon growth conditions. Varying the composition of reaction mixture and temperature, one can change the texture of carbon granule obtained.

CONCLUSION

The experiments showed that methane with inert impurities can be used for synthesis of nanofibrous carbon materials. Thus, the synthesis of nanofibrous carbon can be applied to the wasteless utilization of various diluted hydrocarbon gases (including associated oil gases). However, inert admixtures irreversibly affect the catalytic activity, decreasing the catalyst lifetime and carbon yield.

The self-organization process was observed within a wide range of experimental parameters. It was established, that the texture of obtained carbon nanofibrous granules can be controlled by varying the temperature and concentration of inert impurities in the reaction medium.

Acknowledgement

REFERENCES

1 N. M. Rodriguez , M. S. Kim and R. T. K. Baker, *J. Phys. Chem.*, 98 (1994) 13108.
2 C. A. Frysz, X. Shui and D. D. L. Chung, *J. Power Sources*, 58 (1996) 41.
3 G. A. Kovalenko, E. V. Kuznetsova, Yu. I. Mogilnykh *et al.*, *Carbon*, 39 (2001) 1033.
4 G. G. Kuvshinov, Yu. L. Mogilnykh and M. Yu. Lebedev, R'99 World Congress, Geneva, 1999, vol. 2, p. 199.
5 K. P. De Jong and J. W. Geus, *Catal. Rev.-Sci. Eng.*, 42 (2000) 481.
6 V. I. Zheivot, E. M. Moroz, V. I. Zaikovskii *et al.*, *DAN*, 343 (1995) 781.
7 G. G. Kuvshinov, Yu. I. Mogilnykh, D. G. Kuvshinov *et al.*, *Carbon*, 37 (1999) 1239.
8 N. M. Rodriguez, *J. Mater. Res.*, 8 (1993) 3233.
9 Sh. K. Shaikhutdinov, L. B. Avdeeva, O. V. Goncharova *et al.*, *Appl. Catal. A: General*, 126 (1995) 125.
10 M. A. Ermakova, D. Yu. Ermakov, G. G. Kuvshinov and L. M. Plyasova, *J. Catal.*, 187 (1999) 77.
11 V. V. Chesnokov, R. A. Buyanov, *Russ. Chem. Rev.*, 69 (2000) 623.
12 V. V. Chesnokov, R. A. Buyanov, V. V. Molchanov *et al.*, Pat. 2086502 RF, 1997.
13 G. G. Kuvshinov, Yu. I. Mogilnykh, D. G. Kuvshinov *et al.*, *Carbon*, 36 (1998) 87.
14 G. G. Kuvshinov, Yu. I. Mogilnykh and D. G. Kuvshinov, *Catal. Today*, 42 (1998) 357.
15 A. I. La Cava, C. A. Bernardo and D. L. Trimm, *Carbon*, 20 (1982) 219.
16 J. Rostrup-Nielsen and D. L. Trimm, *J. Catal.*, 48 (1977) 155.
17 M. A. Ermakova, D. Yu. Ermakov, L. M. Plyasova and G. G. Kuvshinov, *Catal. Lett.*, 62 (1999) 93.