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Carburisation of nanocrystalline iron with ethylene

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The carburisation of nanocrystalline iron with ethylene has been studied. The carburisation processes were carried out under atmospheric pressure, under the flow of pure ethylene or ethylene–hydrogen mixture at a constant temperature in the range of 310–550 °C. The process was controlled using a spring thermobalance and cathetometer, with the accuracy of 0,1 mg. The phase composition of the samples after carburisation was determined by means of X-ray diffraction (XRD). As a result of the carburisation of nanocrystalline iron with ethylene, the formation of iron carbide Fe_3C occurs, followed by the formation of carbon deposits. Under a C_2H_4/H_2 gas mixture, these two reaction steps can be separated, while under pure ethylene the reactions are much faster and the simultaneous formation of iron carbide and carbon deposits is observed. Depending on temperature and on the carburisation degree, various forms of carbon deposits can be observed using TEM: spherical, helicoidal, and nanotubes. The diameter of these carbon forms is below 100 nm.

Key words: *nanocrystalline iron; carburisation; ethylene; iron carbide; carbonaceous deposit*

1. Introduction

Carbonaceous deposits formed during industrial processes using hydrocarbons causes the deactivation of catalysts [1–3]. As a consequence, the regeneration or exchange of the deactivated catalyst is necessary. On the other hand, carbon deposits formed on metals as fibres or nanotubes have a lot interesting applications [4–11]. The best catalysts for the preparation of such nanocarbon materials are based on iron, nickel and cobalt [12–31].

This paper deals with the preparation of nanocarbon materials by the decomposition of ethylene on nanocrystalline iron.

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2. Experimental

The nanocrystalline iron used in carburisation experiments was doped with small amounts of two (Al_2O_3 and CaO) or three (Al_2O_3, CaO and K_2O) structural promoter oxides. The samples were obtained by the fusion of magnetite with promoter oxides. The alloy obtained was crushed after cooling and sieved to separate the fraction of 1.2–1.5 mm. To obtain metallic iron, polythermal reduction with hydrogen was performed. The pyrophoric samples obtained after reduction were passivated using nitrogen with an addition of 0,5% of oxygen. The chemical composition after passivation was determined using inductively coupled plasma atomic emission spectroscopy (AES-ICP). Besides iron, the samples contained 2.9 wt. % of Al_2O_3, 3.0 wt. % of CaO, 0.7 wt. % of K_2O, 0.3 wt. % of SiO_2, and 1 wt. % of other metal oxides (Mg, Ni, Cr, Ti, V).

The average crystallite size of iron in the samples, determined using X-ray diffraction (XRD) ($CoK_{\alpha 1}$), and calculated using Scherrer's equation, amounted to 17 nm.

The carburisation process was carried out in a spring thermobalance. A single layer of grains of the sample was placed in a platinum basket and hung in the thermobalance. Changes in the sample mass were recorded with a cathetometer. The accuracy of the measurements was 0.1 mg. Before carburisation, the samples were reduced at a temperature rising from 20 to 500 °C under hydrogen. After reduction (when a constant mass of the sample was reached), the carburisation process was started using ethylene (40 dm^3/h) or an ethylene/hydrogen mixture (1:19). The carburisation processes were carried out isothermally, at a temperature in the range of 310–550 °C.

3. Results and discussion

Examples of the thermogravimetric lines (TG) for the carburisation of nanocrystalline iron with ethylene are shown in Figure 1a. Line (1) corresponds to the carburisation of the sample with a potassium addition, carried out under a mixture of ethylene and hydrogen (1:19). The two other lines correspond to carburisation under pure ethylene – line (2) corresponds to the sample without potassium and line (3) to the one with a potassium added. The carburisation processes were carried out up to a sample mass increase of 0.072 g C/g Fe, which corresponds to the stoichiometric content of carbon in the iron carbide (Fe_3C). In Figure 1b, the derivatives of the TG lines in Figure 1a are shown. Comparing the rates of carburisation under pure ethylene for the two samples – with and without addition of potassium – it can be concluded that the presence of potassium increases the reaction rate. The dilution of ethylene with hydrogen leads to a decrease of the reaction rate (line (1) in Fig. 1b). The reaction rate under a mixture of ethylene with hydrogen for the sample with potassium, however, is higher than the reaction rate on the sample without potassium under pure ethylene.

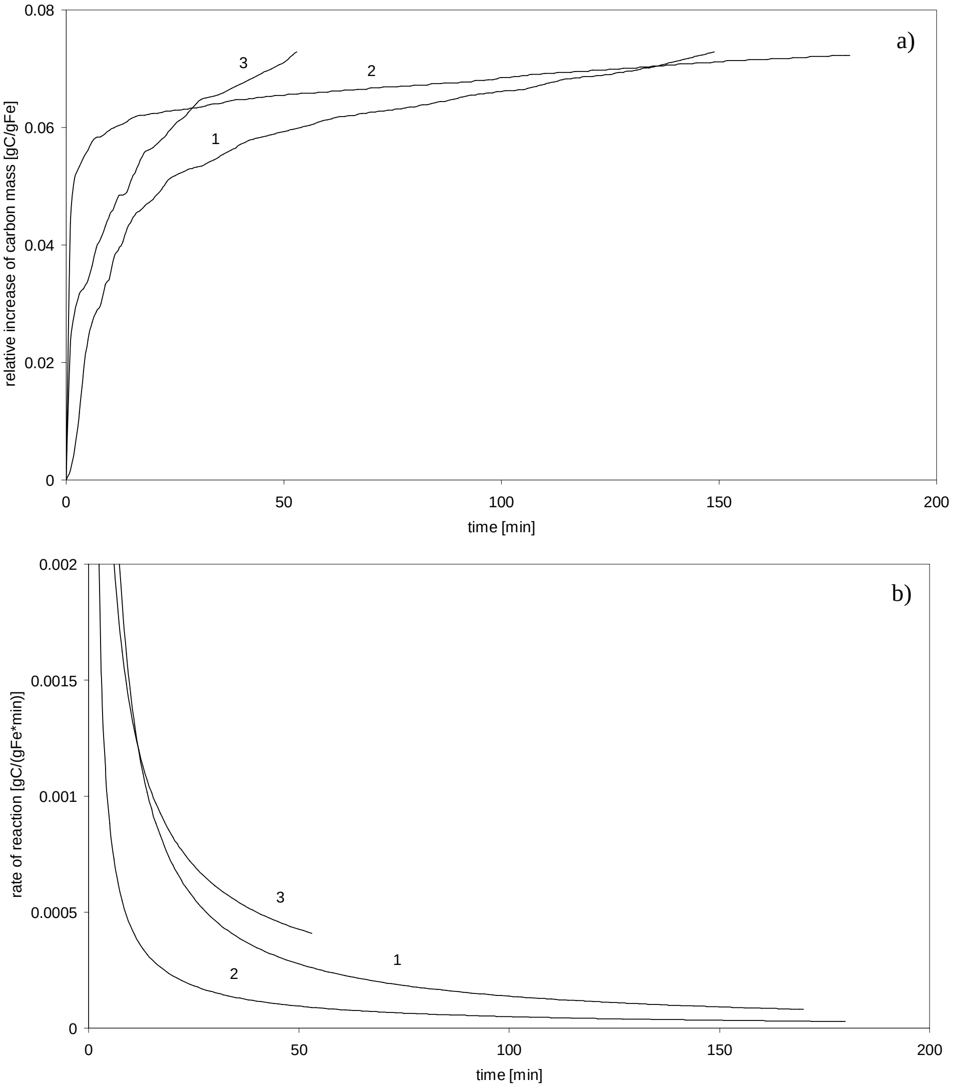

Fig. 1. TG (a) and corresponding DTG (b) curves of the carburisation process of nanocrystalline iron at 370 ºC: 1 – a sample of iron with an addition of potassium, carburised under a C_2H_4/H_2 mixture, 2 – a sample of iron without an addition of potassium, carburised under C_2H_4, 3 – a sample of iron with an addition of potassium, carburised under C_2H_4

The phase composition of the carburised samples was determined using XRD. The results are shown in Figure 2. The number of patterns corresponds to the number of samples in Figure 1. In pattern 4, corresponding to the sample before carburisation, only the peaks corresponding to α-Fe are present. The other peaks visible in patterns 1–3 correspond to iron carbide Fe_3C (cementite). Other iron carbides were not detected.

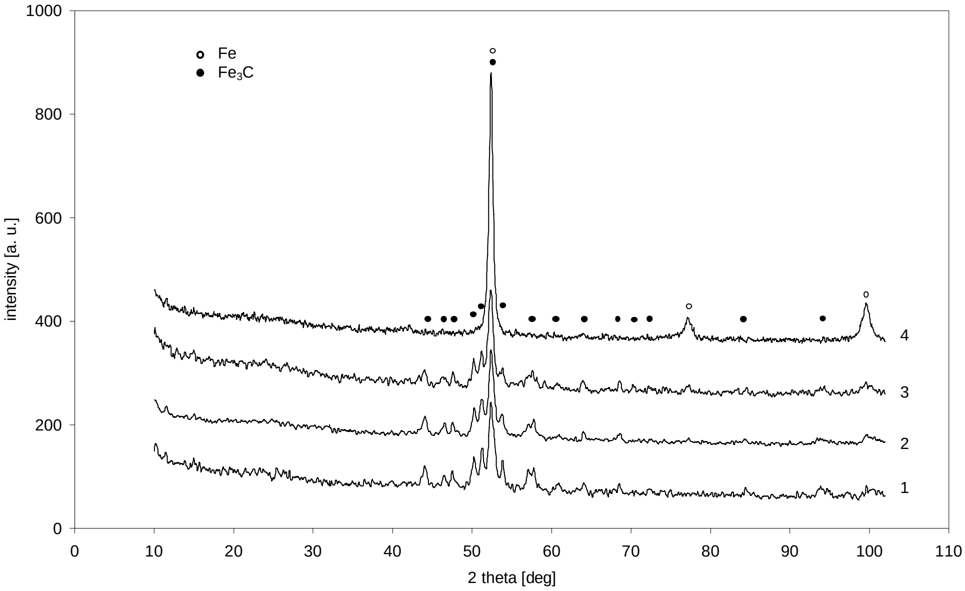

Fig. 2. Diffraction patterns: 1 – triply promoted iron sample after carburisation under a C_2H_4/H_2 mixture, 2 – doubly promoted iron sample after carburisation under C_2H_4, 3 – triply promoted iron sample after carburisation under C_2H_4, 4 – iron sample before carburisation

All samples were carburised to a mass increase corresponding to the amount of carbon sufficient to transform iron into Fe_3C. However, the peaks of unconverted iron can still be observed in the XRD patterns of samples 2 and 3. If free iron is still present in these samples, in spite of the fact that this amount of carbon is sufficient to transform all of the iron into Fe_3C, then carbon deposits have to be formed. Comparing the patterns of these samples, it can be stated that the intensity of the α-iron peak is higher for the sample 3 (with potassium), therefore the formation of carbon deposits occurs earlier on this sample.

In order to determine the range of carbon concentration in which only iron carbide without carbon deposits is formed, the following experiments were carried out. A series of samples with different carbon contents, below the stoichiometric carbon concentration in cementite, was prepared. The phase composition of these samples was determined using XRD. The conversion degree of iron to Fe_3C for each sample was determined on the basis of the surface area of the Fe (200) and Fe_3C (121/210) peaks.

In Figure 3a, the dependences of the conversion degree of iron to Fe_3C on the carbon content are shown for doubly and triply promoted iron samples carburised under pure ethylene at 340 °C. The solid line in this plot corresponds to stoichiometric cementite. For the doubly promoted sample, there are no experimental points below about 0.045 g C/g Fe, since such a substantial mass increase on this sample was measured in a very short period of time at the beginning of the process (during the first 2 minutes). This was the reason for which it was impossible to measure the mass increase for a less carburised sample. For the triply promoted iron sample, it was possible to obtain a sample with lower carbon content, namely 0.03 g C/g Fe. All of the experimental points for both doubly and triply promoted samples are located below the theoretical straight line corresponding to the formation of cementite. Therefore it can be concluded that for carburisation carried out under pure ethylene at 340 °C both cementite and carbon deposits are formed even at the very beginning of the process.

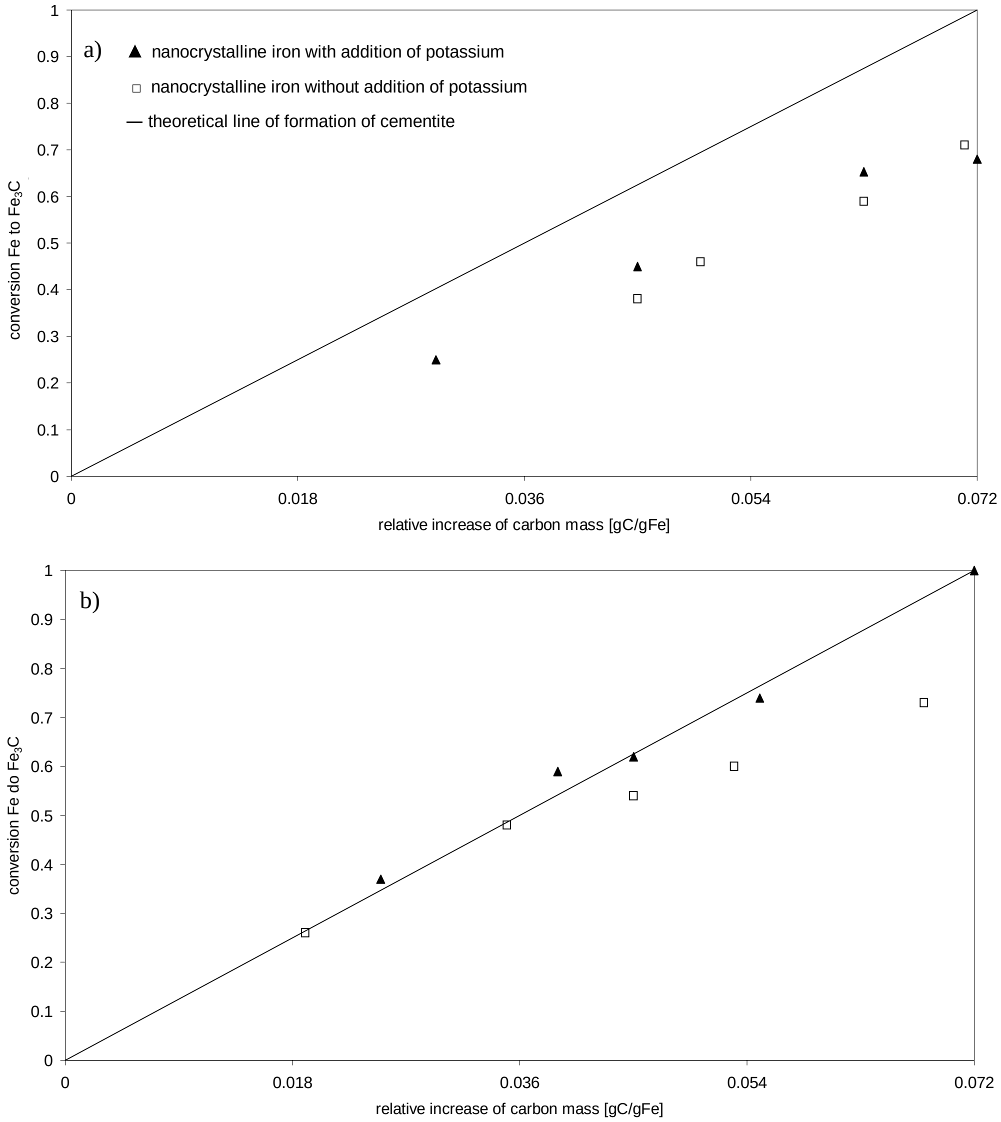

Fig. 3. The dependence of the conversion degree of iron to Fe_3C on the relative increase of carbon mass for: a) doubly and triply promoted iron samples, carburised under pure ethylene at a temperature of 340 °C; b) doubly (at 340°C) and triply (at 370°C) promoted iron samples, carburised under a mixture of ethylene/hydrogen (1:19)

In Figure 3b, a similar dependence is shown for carburisation under a mixture of ethylene with hydrogen (1:19) for the doubly promoted iron sample at 340 °C and for the triply promoted sample at 370 °C. The experimental points for the triply promoted sample are located on the line corresponding to the cementite formation, thus under the conditions of this experiment only cementite is formed, without carbon deposits. The experimental points for the doubly promoted sample are also located on the cementite line, but only below a mass increase of about 0.04 g C/g Fe. Above this value, the experimental points are located below the theoretical cementite line, therefore carbon deposits are then formed simultaneously with cementite.

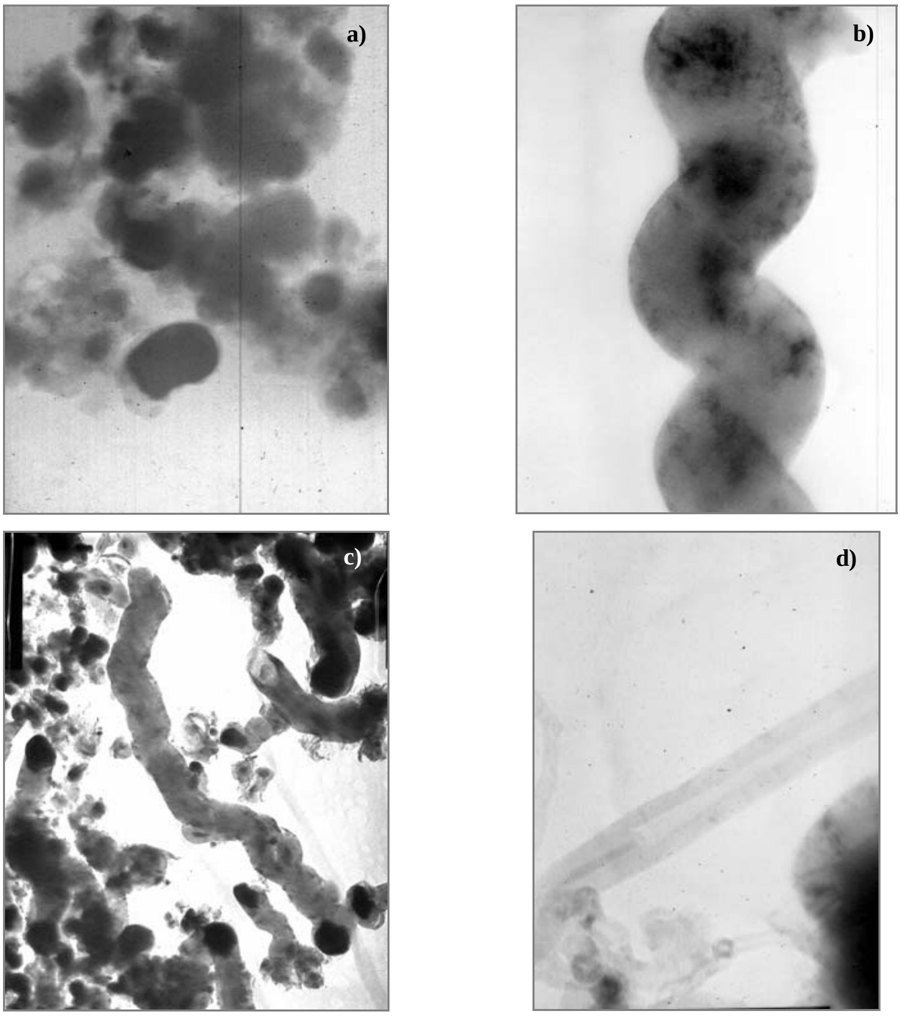

Fig. 4. TEM images of the sample: a) without addition of potassium, carburised under C_2H_4 at of 450 °C; b) without the addition of potassium, carburised under C_2H_4 at 500 °C, c) with the addition of potassium, carburised under C_2H_4 at 550 °C; d) without addition of potassium, carburised under C_2H_4 at the temperature of 550 °C

In order to identify the forms of carbon deposits, a series of samples carburised under pure ethylene for 180 min was prepared. The samples obtained were characterised using TEM. In Figure 4a, TEM image is presented of a doubly promoted iron sample carburised at 450 °C, up to a mass increase of about 0.9 g C/g Fe. Spherical carbon forms 10–20 nm in diameter can be observed.

Fibrous forms of carbon deposits were observed after carburisation to a higher degree (1.7 g C/g Fe) and at higher temperature (500 °C). Under these experimental conditions, carbon fibres about 100 nm in diameter were obtained (Fig. 4b). Figure 4c shows a TEM image of the iron sample containing potassium carburised at 550 °C up to a mass increase of 1.32 g C/g Fe. At the end of the carbon fibres, iron carbide crystallites about 100 nm in diameter can be observed. The diameter of the carbon fibres in this picture is in the range 50–150 nm. Similar carbon structures were observed on the doubly promoted iron sample carburised at the same temperature up to 1.24 g C/g Fe. Hollow carbon fibres were also observed in this case (Fig. 4d). The external diameter of these fibres was about 40 nm and the internal one about 10 nm.

There were no differences in the forms of carbon deposits obtained on the doubly and triply promoted iron samples.

4. Conclusions

The products of the carburisation of nanocrystalline iron with ethylene are iron carbide and carbon deposits. Iron carbide is formed only as cementite, other iron carbides were not detected.

The presence of potassium in the sample enhanced the reaction rate.

The form of carbon deposits depends on the process conditions. In the temperature range of 500–550 °C, carbon fibres are formed.

References

[1] FORZATTI P., LIETTI L., Catal. Today, 52 (1999), 165.
[2] GÓRALSKI J., GRAMS J., LUDOMIRSKA I., PARYJCZAK T., RZEŹNICKA I., Przem. Chem., 5 (1999), 172.
[3] GÓRALSKI J., GRAMS J., LUDOMIRSKA I., PARYJCZAK T., RZEŹNICKA I., Wiad. Chem., 54 (2000), 591.
[4] DE JONG K.P., GEUS J.W., Catal. Rev. Sci. Eng., 42 (2000), 481.
[5] LIPKA S.M., Annu. Battery Conf. Appl. Adv., 13 (1998), 373.
[6] PARK C., ENGEL E.S., CROWE A., GILBERT T.R., RODRIGUEZ N.M., Langmuir, 16 (2000), 8050.
[7] BROWNING D.J., GERRARD M.L., LAKEMAN J.B., MELLOR I.M, MORTIMER R.J., TURPIN M.C., Proc. Power Sources, Conf, 39 (2000), 192.
[8] SEUK YOUN H., RYU H., CHO T., CHOI W., Intern. J. Hydr. Energy, 27 (2002), 937.
[9] HWANG J., LEE S., SIM K., KIM J., Synth. Met., 126 (2002), 81.
[10] PHAM-HUU C., KELLER N., RODDATIS V.V., MESTL G., SCHLOEGL R., LEDOUX M.J., Phys. Chem. Chem. Phys., 4 (2002), 514.
[11] QIAN W., LIU T., WEI F., WANG Z., YU H., Carbon, 41 (2003), 846.
[12] EMMENEGGER C., BONARD J.M., MAURON P., SUDAN P., LEPORA A., GROBETY B., ZÜTTEL A., SCHLAPBACH L., Carbon, 41 (2003), 539.

[13] FAZLE KIBRIA A.K.M., MO Y.H., NAHM K.S., KIM M.J., Carbon, 40 (2002), 1241.

[14] VENEGONI D., SERP P., FEURER R., KIHN Y., VAHLAS C., KALCK P., Carbon, 40 (2002), 1799.

[15] PARK C., BAKER R.T.K., J. Catal., 179 (1998), 361.

[16] ANDERSON P.E., RODRIGUEZ N.M., Chem. Mater., 12 (2000), 823.

[17] MARANGONI R., SERP P., FEURER R., KIHN Y., KALCK P., VAHLAS C., Carbon, 39 (2001), 443.

[18] OTSUKA K., OGIHARA H., TAKENAKA S., Carbon, 41 (2003), 223.

[19] LOPEZ P.N., RAMOS I.R., RUIZ A.G., Carbon, 41 (2003), 2509.

[20] BAKER R.T.K., BARBER M.A., HARRIS P.S., FEATES F.S., WAITE R.J., J. Catal., 26 (1972), 51.

[21] RODRIGUEZ N.M., KIM M.S., BAKER R.T.K., J. Catal., 144 (1993), 93.

[22] RODRIGUEZ N.M., KIM M.S., FORTIN F., MOCHIDA I., BAKER R.T.K., Appl. Catal. A: General, 148 (1997), 265.

[23] VANDER WAL R.L., Carbon, 40 (2002), 2101.

[24] CI L., XIE S., TANG D., YAN X., LI Y., LIU Z., ZOU X., ZHOU W., WANG G., Chem. Phys. Lett., 349 (2001) 191.

[25] LI Z., CHEN J., ZHANG X., LI Y., FUNG K.K., Carbon, 40 (2002), 409.

[26] ERMAKOVA M.A., ERMAKOV D.Y., KUVSHINOV G.G., Appl. Catal. A: General, 201 (2000), 61.

[27] ERMAKOVA M.A., ERMAKOV D.Y., CHUVILIN A.L., KUVSHINOV G.G., J. Catal., 201 (2001), 183.

[28] QIAN W., LIU T., WANG Z., YU H., LI Z., WEI F., LOU G., Carbon, 41 (2003), 2487.

[29] KRISHNANKUTTY N., RODRIGUEZ N.M., BAKER R.T.K., J. Catal., 158 (1996), 217.

[30] HERNADI K., FONESCA A., NAGY J.B., BERNAERTS D., LUCAS A.A., Carbon, 34 (1996), 1249.

[31] BAKER R.T.K., CHLUDZINSKI J.J., J. Catal., 64 (1980), 464.

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