

Oxidative Dehydrogenation of Ethylbenzene to Styrene over Carbonaceous Materials

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Abstract

The oxidative dehydrogenation of ethylbenzene to styrene was studied over carbon black, graphite, and multi-walled carbon nanofilaments. The catalytic properties of these carbon compounds were compared in order to hopefully determine the carbon structure being most active. Differences were observed in the catalytic behaviors of these carbon materials. Carbon nanofilaments showed a higher catalytic activity and stability for the reaction than carbon black or graphite. Styrene yields were obtained of 42% at ethylbenzene conversions of 62%, and selectivities to styrene of 67%. The catalytic behavior of all carbon catalysts during the reaction could be correlated with the evolution of their specific surface areas during the reaction. This indicates that carbon nanofilaments and graphite are stable catalysts for the oxidative dehydrogenation of ethylbenzene.

Introduction

The production of styrene (ST) monomer from ethylbenzene (EB) is one of the ten largest production processes in chemical industry. It is catalyzed by modified iron oxides in an endothermic dehydrogenation process at high temperatures between 870 and 930 K [1]. Because the commercial dehydrogenation of EB to ST is limited by the thermodynamic equilibrium, energy intensive with an excess of steam [2-3], and accompanied by coke deposition leading to catalyst deactivation, there is a strong incentive for the development of alternative technologies. The oxidative dehydrogenation (ODH) of EB to ST is one of the most promising reactions in this respect, which allows one to realize an exothermic reaction due to water formation as a by-product.

Different compounds, i.e. transition metal oxides [4], phosphates [5-6], and polymers [7], were found to be active and selective catalysts for the ODH of EB to ST. Mechanistic studies with single crystalline model systems [8-9] and investigations of ODH reactions [10] may indicate that the deposited coke may not be detrimental for the reaction as often sug-

gested. In contrast, coke may even be the active catalyst species in the reaction. Moreover, the fact that different, mainly oxide-based substances, tend to coke deposition and are active catalysts for ODH of EB also point to the fact that carbon is probably the active phase common for all ODH catalysts. Hence, it was found that activated carbons are catalytically active for the ODH [11-12]. However, a commercialization of the amorphous carbon as catalyst is not possible due to its low resistance to oxidation [13].

In the present study, the catalytic properties of carbon black, graphite, and multi-walled carbon nanofilaments (MWNFs) were compared for ODH of EB to ST. Time on stream experiments with different stoichiometric ratios of EB and oxygen over carbon black, graphite, and MWNFs were performed to understand the behavior of different carbons as catalysts for ODH of EB to ST.

High resolution transmission electron microscopy (HREM), X-ray photoelectron spectroscopy (XPS), and BET specific surface area analyses of the fresh and used samples were compared with the catalytic activity of carbon black, graphite, and MWNFs for ODH of EB to ST to hopefully understand the nature of the active species.

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Experimental

Carbon black – Lamp Black 101 (Degussa), a natural graphite – “AF spezial” (Kropfmühl), and commercial MWNFs (Applied Science Ltd) were used in this study. The catalytic reaction was carried out in quartz tubular flow reactors of 4 mm inner diameter and 200 mm length. Catalyst particles (0.02 g) were held in the isothermal oven zone between two quartz wool plugs. He and O₂ were fed through mass flow controllers (Bronkhorst). The EB was evaporated at 308 K (2,16 kPa) in flowing He and mixed with the O₂ flow in EB to oxygen ratio 1 to 1. The reaction was performed at 820 K with a total flow of 10 ml/min giving a liquid hourly space velocity (LHSV) of 0.5 h⁻¹. The hydrocarbon products were analyzed by an one-line gas chromatograph equipped with a 5% SP-1200/1.75% Bentone 34 packed column and an FID detector. The permanent gases were analyzed simultaneously using a Carboxen 1010 PLOT column and a TCD detector.

The parameters of the catalytic activity were defined by the following equations:

$$\text{EB conversion: } X = \frac{F_{EBin} - F_{EBout}}{F_{EBin}} \times 100\%$$

$$\text{ST yields: } R_{ST} = \frac{F_{ST}}{F_{EBin}} \times 100\%$$

$$\text{Selectivity to ST: } S_{ST} = \frac{F_{ST}}{F_{EBin} - F_{EBout}} \times 100\%$$

with “F” being the respective percent concentration of the different gases and the subscripts, “in” and “out”, the respective percent of the feed and outlet. The relative yields of co-products were calculated by the same way.

The HREM characterization of the carbon materials before and after catalytic tests was made on a Phillips CM200 Field Emission Gun electron microscope operated at 200kV. Photoelectron spectra were obtained using a modified Leybold Heraeus spectrometer (LHS12 MCD) with Mg K_α radiation (1253.6 eV) at 240 W power. The bandpass energy was set to 50 eV. The spectra were evaluated after satellite subtraction and subtraction of a Shirley background. The binding energy scale was calibrated using a binding energy of Au 4f_{7/2} of 84.0 eV. The surface area of the catalyst was measured with the BET method using

liquid nitrogen as adsorbate.

Results and discussion

Figure 1a shows the evolution of the ST yield, EB conversion, and selectivity to ST over carbon black with time on stream for the anaerobic dehydrogenation of EB to ST. A slight initial decrease of activity was observed. The ST yield was about 12% at a EB conversion of 22% and a selectivity to ST of 55% under steady state. With oxygen added to the feed, the initial ST yield was 64% at a EB conversion of 82% and a selectivity to ST of 78% (Fig. 1b). Subsequently, a decrease of the activity was observed during 160 min. Under steady state, the ST yield was 34%, the EB conversion and the selectivity to ST were 66 and 52%, respectively.

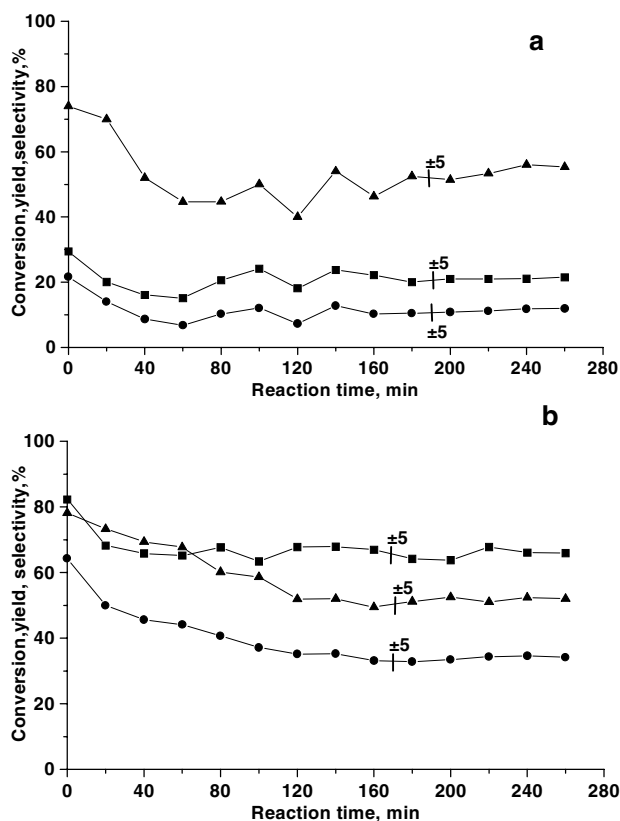


Fig. 1. Catalytic performance of carbon black under (a) anaerobic and (b) oxidative dehydrogenation of ethylbenzene to styrene at 820 K with time on stream. (■) EB conversion; (▲) selectivity to ST; (●) ST yield.

In Fig. 2a, a typical profile is shown of the reaction in absence of oxygen for graphite as catalyst. A slight initial deactivation and subsequent activation was observed in the EB conversion data. The

behavior is reflected in the ST selectivity, which goes through a maximum at short times on stream. Under steady state, the ST yield was 11% at a EB conversion of 23% and a selectivity to ST of 47%. With oxygen added to the feed, the activity of graphite was almost constant with ST yields of 26% at an EB conversion of 49% and a selectivity to ST of 54% (Fig. 2 b).

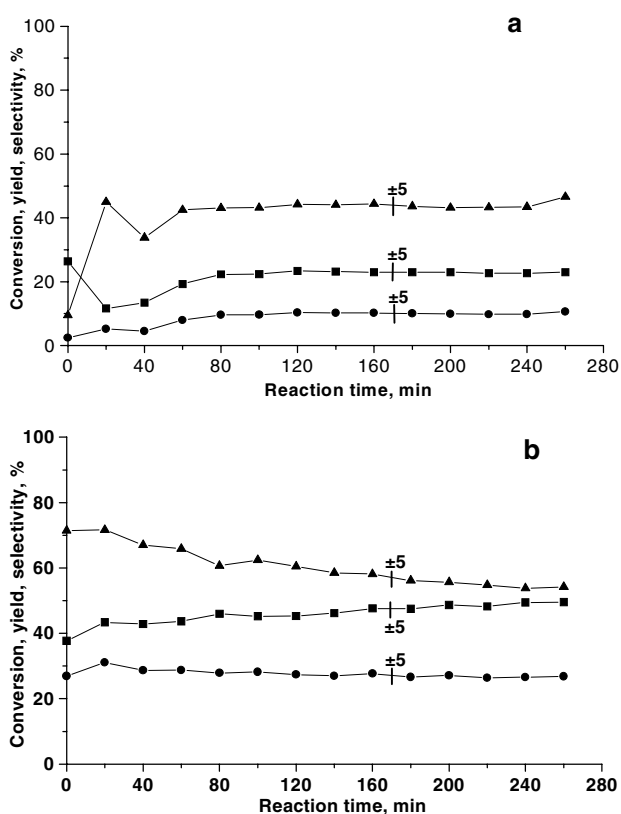


Fig. 2. Catalytic performance of graphite under (a) anaerobic and (b) oxidative dehydrogenation of ethylbenzene to styrene at 820 K with time on stream. (■) EB conversion; (▲) selectivity to ST; (●) ST yield.

Fig. 3 depicts the catalytic behavior of MWNFs in these reactions. An initial activation was observed for MWNFs in the absence of oxygen. After the initial activation, the ST yield was 14% at a EB conversion of 30% and a selectivity to ST was 49% under steady state (Fig. 3 a). After the initial activation period and in presence of oxygen, the ST yield was 42% at a EB conversion of 62% and a selectivity to ST of 67% (Fig. 3 b).

The catalytic results of ODH of EB over carbon black, graphite, and MWNFs are summarized in Table 1. The summarized catalytic parameters were calculated after the induction period when the apparent steady states were reached. A comparison shows

that the MWNFs exhibited higher ST yield, EB conversion, and selectivity to ST than carbon black and graphite catalysts.

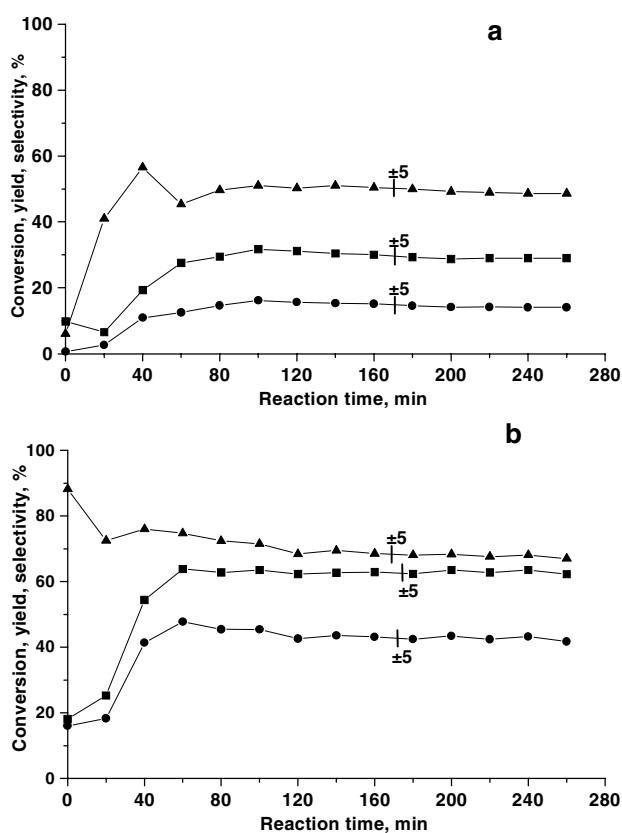


Fig. 3. Catalytic performance of carbon nanofilaments under (a) anaerobic and (b) oxidative dehydrogenation of ethylbenzene to styrene at 820 K with time on stream. (■) EB conversion; (▲) selectivity to ST; (●) ST yield.

Table 1

Activity of the various carbons in the oxidative dehydrogenation of ethylbenzene to styrene*

Sample	Styrene yield (%)	Ethylbenzene conversion (%)	Selectivity to styrene (%)
Carbon black	34±5	66±5	52±5
Graphite	26±5	49±5	54±5
MWNFs	42±5	62±5	67±5

*At steady state after first 160 min; T=820 K; LHSV 0.5 h⁻¹; ethylbenzene to oxygen ratio 1 to 1.

Table 2 shows a comparison of the evolution of the catalytic activity of the tested carbons, their stabilities toward oxidation, and their specific surface areas before and after the reaction. The observed decreasing activity of carbon black thus could be correlated with the decrease of the specific surface

area from 26 to 19 m²/g. Graphite has shown almost constant activity during the experiments which is accordingly correlated with its almost constant specific surface area. An increase of the activity of MWNFs during the initial stage of reaction could be correlated with the increase of their specific surface area.

Experiments on the time dependency of the

catalytic activity under the conditions mentioned above revealed that carbon black is not stable for ODH of EB. It was completely oxidized during 12 hours time of operation. Under the same conditions, only 25% of the graphite were oxidized. MWNFs have shown a still higher stability toward oxidation than graphite (Table 2).

Table 2

Comparison of initial activity, weight loss of the samples after 12 hours on stream at 820 K, and specific surface area of the samples before and after the reaction for ODH with different carbons.

Sample	Activity during an initial stage	Weight loss after 12 h on stream, %	BET before reaction, m ² /g	BET after 7 h on stream, m ² /g
Carbon black	Decreasing	100	26	19
Graphite	Constant	25	11	13
MWNFs	Increasing	15	26	47

A HREM image of the MWNF sample is shown in Fig. 4. MWNFs and chain-like filaments were observed with diameters in the range of 50 – 500 nm and a length from 100 nm to a few microns. A systematic HREM study revealed that the walls of the MWNFs consisted of two layers as shown in Fig. 5 a. The filaments are built up first by an inner layer of conical graphite layers. The angle of the inclination of graphite layers to the nanofilament axis is about 26° and their interplane distance is 0.348 nm which is similar to that of graphite. The second outer nanofilament shell is formed by amorphous carbon layers, which are oriented parallel to the tube axis. The average distance between the layers was determined to be about 0.388 nm.

HREM and energy dispersive X-ray (EDX) investigations of the carbon nanofilament sample showed that they contain pure metallic iron covered by graphite layers. Traces of iron carbides or oxides have not been observed.

In Fig. 5b, the wall of a carbon nanofilament is shown after 20 hours time on stream. The HREM images indicate that the outer second shell of more amorphous carbon layers has disappeared, but the wall of the nanofilament was still covered by amorphous carbon, especially at the step edges between the conical graphene sheets. In addition, the ends of the inner conical layer seem to be partially oxidized. Systematic HREM observations have shown the absence of the Fe particles not covered by carbon layers. The

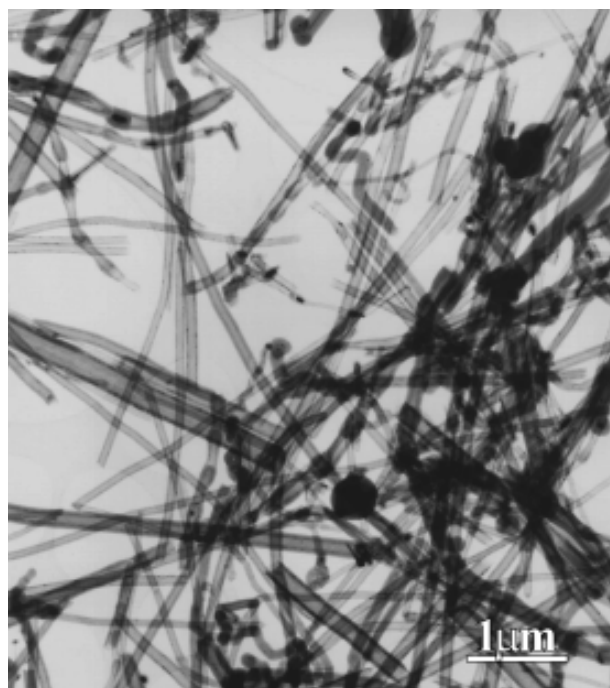


Fig. 4. Representative HREM image of the sample of carbon nanofilaments before the reaction.

burning off of carbon layers of MWNFs during the reaction did not lead to uncovered Fe particles. It proves that Fe particles did not take part in the reaction.

The C 1s XP spectra of the carbon nanofilaments before and after the reaction are shown in Fig. 6. The major C 1s signal with a binding energy of 284.8 eV

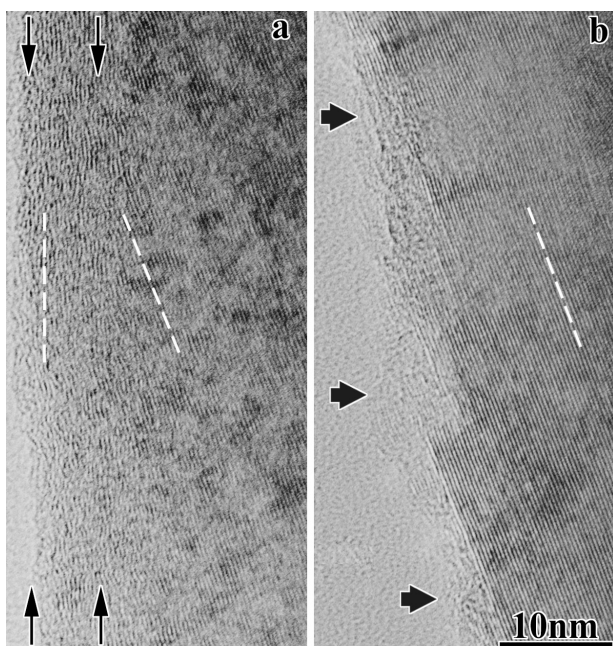


Fig. 5. HREM image of the wall of a carbon nanofilament. (a) before the reaction and (b) after 20 hours on stream with twice the stoichiometric excess of oxygen.

is assigned to graphitic sp^2 carbon. The asymmetry of the peak toward higher binding energies is characteristic for the presence of oxygenated surface groups, e.g. carbonyls, quinones, hydroxyls [14]. A detailed deconvolution of all the contributions was not attempted due to the arbitrariness of such a multisignal deconvolution. However, XPS proved the presence of at least two different carbon species on the surface of the fresh sample (Fig. 6a, and inset). The second species has a binding energy of about 286 eV and is attributed to carbon atoms oxygen containing surface groups, c.g. OH. After reaction (Fig. 6b), the signal intensity of these groups has strongly decreased relative to that of the graphitic carbon. This indicates their preferential burn-off during the reaction.

Fig. 7 displays the O 1s XP spectra recorded of the nanofilaments prior and subsequent to the catalytic reaction. The decrease of the oxygen content was also confirmed by the O 1s XP signals. Oxygen-containing functional groups could be observed before the reaction (Fig. 7, a). After the reaction (Fig. 7, b), only a weak O1s signal was detected at 533.6 eV, which indicates a decrease of the content of C-O functional surface groups. This result implies that the C-O species may actively take part in the catalytic ODH. It is suggested that the catalytic ODH reaction takes place at some, still unknown active surface sites

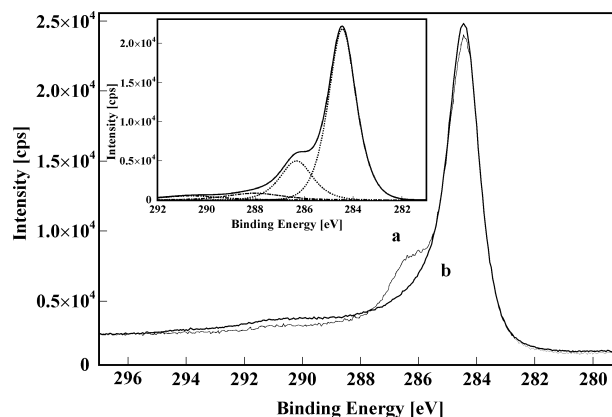


Fig. 6. Carbon 1s core level spectra of carbon nanofilaments. (a) and inset before the reaction, (b) after the reaction.

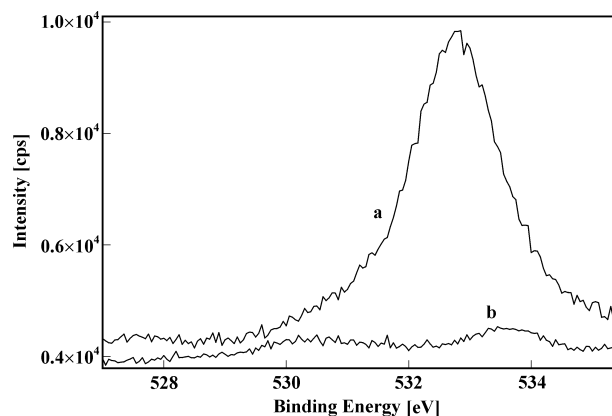


Fig. 7. Oxygen 1s core level spectra of carbon nanofilaments. (a) before the reaction and (b) after the reaction.

on the graphene-like layers of the nanofilaments.

Conclusion

It can be concluded from a comparison of the obtained results that the active carbon species are formed during the initial reaction period on the carbon surface. The carbon surface itself most probably acts as a host for the active species, which may react with EB under the abstraction of hydrogen and the formation of ST and water. In case of amorphous carbon black, a multitude of oxygenated species is present on the carbon surface from the very beginning of the reaction. During the initial reaction period of 160 min on stream, these oxygenated carbon burned off as proven by the loss of specific surface area. Hence, the catalytic activity of activated carbon decreased with time on stream. The catalytic activity of graphite was almost constant during the reaction. This could be correlated with the almost constant BET surface area. Additionally, the high crystallinity of this sample

and the absence of oxygenated carbon surface groups suggest that intact graphene layers may play an important role in the ODH of EB. This is in line with the observed activity of intact graphite for the selective oxidation of methanol [15]. In case of MWNFs, the initial catalytic activity was low. The activity increased during the induction period to reach steady state. This can be correlated with the increasing BET surface area after the reaction. Moreover, this observation sheds light on the role of amorphous and graphene-like carbons in the ODH. The MWNFs were initially completely covered by a shell of amorphous carbon. After reaction, this shell has been burned off. Hence, it may be concluded that high catalytic activity only developed after this amorphous shell was removed and the graphene layers were accessible to the gas phase.

Carbon is active for the oxidative dehydrogenation of ethylbenzene to styrene. Carbon nanofilaments have shown a higher activity with higher selectivities to styrene in the oxidative dehydrogenation of ethylbenzene to styrene. They also showed a higher resistance toward oxidation in comparison with carbon black and graphite. This proves that carbon nanofilaments could be used as an active and selective catalyst for the oxidative dehydrogenation of ethylbenzene to styrene.

However, the nature of the surface carbon species formed during the reaction, which are active for the oxidative dehydrogenation of ethylbenzene to styrene, still remains unidentified and will be the matter of future investigations.

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References

1. D.H. James, W.M. Castor, Ullmann's Encycl. 5th Ed., Vol. 25 (Ind.Chem. 1994) pp 329-344.
2. J. Matsui, Appl. Catal., 51 (1989) 203.
3. F.Cavani, F. Trifiro, Appl. Catal. A: General, 133 (1995) 219.
4. Z. Dziejewicki, A. Makowski, React. Kinet. Catal. Lett., 13 (1980) 51.
5. G. Emig, H. Hofmann, J. Catal., 84 (1983) 15.
6. G.E. Vrieland, P.G.Menon, Appl. Catal., 77 (1991) 1.
7. G. C Grunewald, R.S. Drago, J. Mol. Catal., 58 (1990) 227.
8. M. Muhler, J. Schütze, M. Wesemann, T. Rayment, A. Dent, R. Schlögl, G. Ertl, J. Catal. 126 (1990) 339.
9. M. Muhler, R. Schlögl, G. Ertl, J. Catal. 138 (1992) 413.
10. W. Ogranowski, J. Hanuza, L. Kepinski, Appl. Catal. A 171 (1998) 145.
11. T.G. Alkhazov, Kinet. Katal. 13 (1972) 509.
12. M.F.R. Pereira, J.J.M. Orfao, J.L. Figueiredo, Appl. Catal. A 184 (1999) 153.
13. M.F.R. Pereira, J.J.M. Orfao, J.L. Figueiredo, Appl. Catal. A 196 (2000) 43.
14. H. Ago, T. Kugler, F. Cacialli, W.R. Salaneck, M.S.P. Shaffer, A.H. Windle, R.H. Friend, J.Phys.Chem. B 103 (1999) 8116.
15. E. Sanchez-Cortezon, G. Mestl, M. Schur, R. Schlögl, Appl. Catal. (in press).

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