Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Catalysis 240 (2006) 18–22

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Bimetallic catalysis on carbon nanotubes for the selective hydrogenation of cinnamaldehyde

Hung Vu [a], Filomena Gonçalves [a], Régis Philippe [a], Emmanuel Lamouroux [a], Massimiliano Corrias [a], Yolande Kihn [b], Dominique Plee [c], Philippe Kalck [a], Philippe Serp [a,*]

[a] *Laboratoire de Catalyse, Chimie Fine et Polymères, Ecole Nationale Supérieure d'Ingénieurs en Arts Chimiques Et Technologiques, 118 Route de Narbonne, 31077 Toulouse cedex 4, France*

[b] *CEMES-CNRS n°8001, 2 rue Jeanne Marvig 31055 Toulouse, France*

[c] *Arkema, Groupement de Recherches de Lacq, BP 34, 64170 Lacq, France*

Received 10 January 2006; revised 3 March 2006; accepted 6 March 2006

Abstract

Carbon nanotube-based catalysts (Pt, Ru, and Pt–Ru) were developed and compared with their analogues on activated carbon for the selective reduction of cinnamaldehyde to the corresponding unsaturated alcohol. The use of a mesoporous nanostructured support, which makes mass transfer limitations less significant, gave far better activities than microporous activated carbon. A bimetallic system was found to afford a remarkably high selectivity (93%) for high conversion levels (80%), provided that a thermal pretreatment was performed on the catalyst. These results can be rationalized in terms of electron transfer from the support to the metal.

Keywords: Carbon nanotubes; Cinnamaldehyde hydrogenation; Bimetallic catalysts; Metal–support interaction; Platinum catalyst

1. Introduction

Carbon materials are attractive supports in heterogeneous catalytic processes because of their properties that may be tailored to specific needs [1,2]. With the discovery of nanometer-scale fibrous carbon morphologies and the large-scale synthesis of such structures, much attention is being focused on their potential applications to various fields of materials science, such as composite elaboration, electronics, and catalysis [3]. In particular, these materials have excellent electronic properties, good chemical stability, and large surface areas, making them promising supports for advanced catalytic systems. Nanostructured carbon materials have already been successfully used in heterogeneous catalysis [4], but, unfortunately, a lack of systematic comparison with traditional activated carbon-supported catalysts is evident. Moreover, there have been few studies [5] dealing with the comparison of catalysts prepared on different types of carbon nanotubes and nanofibers, namely multi-walled carbon nanotubes (MWNTs), single-walled carbon nanotubes (SWNTs), and graphite nanofibers (GNFs). We have chosen the selective hydrogenation of cinnamaldehyde (CAL) reaction to study the influence of the carbon support (MWNT, GNF, SWNT, and commercial activated carbon [AC]) on the catalytic performances of monometallic and bimetallic catalysts. The selective hydrogenation of the carbonyl group of the above α,β-unsaturated aldehyde, yielding the unsaturated alcohol, remains a challenging task and is of particular interest because of the importance of such alcohols in the fine chemicals industry [6]. Group 8–10 metal catalysts have been tested in CAL hydrogenation, and Pd and Rh generally display high activity but rather poor selectivity toward cinnamyl alcohol; Pt and Ru, the most commonly used metals, exhibit moderate selectivity [6]. Among other factors, selectivity could be enhanced by the electronic effects of the support, the presence of a second metal, and the metal particle sizes and morphology [6]. Considering the better selectivity presented by Pt and Ru catalysts, these metals were used as active phases. In this study, we present novel important results obtained, in terms of activity and selectivity

---

[*] Corresponding author.
E-mail address: Philippe.Serp@ensiacet.fr (P. Serp).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2006.03.003

for the selective hydrogenation of CAL under mild conditions on high-temperature-treated bimetallic catalysts supported on MWNT.

2. Experimental

Nanosized fibrous carbon supports were prepared by catalytic chemical vapor deposition [7] and characterized by XPS, N_2 adsorption isotherms, TEM, and Raman spectroscopy. The high-purity MWNT (98% purity, o.d. 10–22 nm, $S_{\text{BET}} = 196\ \text{m}^2/\text{g}$, $V_{\text{micro}} = 0.8\ \text{cm}^3/\text{g}$) and GNF (93% purity, o.d. 15–25 nm, $S_{\text{BET}} = 167\ \text{m}^2/\text{g}$, $V_{\text{micro}} = 0.5\ \text{cm}^3/\text{g}$) used in this study comprise mainly mesopores and macropores, whereas activated carbon has a microporous structure with a much higher specific surface area ($700\ \text{m}^2/\text{g}$). The SWNTs used in this study has an intermediate structure. A surface organometallic approach has been followed to deposit platinum and ruthenium on various carbon supports [8] by means of $[\text{Pt}(\text{CH}_3)_2(\eta^4\text{-C}_8\text{H}_{12})]$ [9] and $[\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})(\eta^6\text{-C}_8\text{H}_{10})]$ [10] as precursors. Before metal impregnation, carbon supports were oxidized with HNO_3 to develop oxygen-containing surface groups, which act as anchoring sites for the precursors [4]. The concentration of the metal precursors in the impregnating solutions was calculated to obtain 2% (w/w) of Pt and/or Ru over each support. Two different series of bimetallic catalysts were prepared by varying the impregnation mode; in one mode the metals were introduced simultaneously (PtRu), whereas in the other mode the supports were sequentially impregnated, first by Pt and then by Ru (Ru/Pt). Before the catalytic tests, all catalysts were reduced at 350 °C under H_2 flow. CAL hydrogenation was carried out under 2 MPa of H_2 at 100 °C for 2 h in a 150-mL Hastelloy B2 autoclave. The experiments were carried out in 25 mL of isopropanol with 100 mg of supported catalyst and 2 g of CAL.

3. Results and discussion

The relative amounts of oxygen-containing surface groups were inferred from the oxygen surface concentration determined by X-ray photoelectron spectroscopy (XPS). The AC-supported catalysts showed the highest content of oxygen-containing surface groups (C/O atomic ratio = 85/15), and, among the nanostructured carbon supports, GNF (because of the peculiar orientation of its graphene layers) was the material for which the HNO_3 treatment led to the highest increase in the oxygenated groups (C/O atomic ratio = 90/10). Transmission electron microscopy (TEM) observations showed that highly dispersed metallic particles were obtained over all of the supports, with mean sizes ranging between 1 and 8 nm, depending on the system. Comparing metal particle size distributions determined for monometallic catalysts (Ru and Pt), we found that smaller metal particles were obtained for ruthenium (Ru/MWNT = 1.7 nm; Pt/MWNT = 2.3 nm), possibly due to the higher reactivity of the organometallic Ru precursor that allows better nucleation of nanoparticles. For bimetallic catalysts, higher dispersions were obtained on metals coimpregnation (PtRu/MWNT = 1–3 nm; Ru/Pt/MWNT = 1–7 nm). We could observe that the particle size distributions obtained for the Ru/Pt catalysts were very close to those obtained for the corresponding monometallic Pt systems, thus suggesting that Ru deposition occurs over the Pt sites on the two step-impregnation procedure. For the co-impregnated PtRu catalysts, the mean particle size was smaller than that found for the monometallic platinum system (PtRu/MWNT = 1.8 nm; Pt/MWNT = 2.3 nm). This phenomenon was even more pronounced in the case of AC support (Pt/AC = 5.1 nm; Ru/AC = 1.8 nm; PtRu/AC = 2.4 nm), indicating the importance of the ruthenium precursor reactivity. As for the influence of the support on the dispersion of the active species, we observed that for each catalytic system (Pt, Ru, PtRu, and Ru/Pt), the average particle size follows the sequence GNF $<$ MWNT $\approx$ SWNT $<$ AC. The poor metal dispersions obtained for the catalysts prepared on AC (Pt/AC = 5.1 nm; Pt/GNF = 1.5 nm) might be due to the low reactivity of the platinum precursor with the surface oxygenated groups and to diffusional limitations during the impregnation procedure that can block the access of the metal precursor molecules into the microporous structure of this support. Indeed, TEM micrographs showed a nonhomogeneous distribution of platinum for the Pt/AC sample. For the nanostructured carbon-supported catalysts, the different metal dispersions obtained might be explained by the different amounts of oxygen-containing surface groups; the higher this amount, the better the dispersion. The highest dispersions obtained on GNF-supported catalysts might also be due to the orientation of the graphene layers in this support, which are likely more favorable to nanoparticles anchorage and stabilization [11]. In our case, an angle of 12°–15° was found between the graphene layers and the axis of the GNF; for MWNT, this angle is close to 0° (Fig. 1).

Under the reacting conditions used, the main products of CAL hydrogenation (Scheme 1) were cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL). Table 1 lists conversions and selectivities toward COL obtained over the different catalysts. Whatever the nanostructured carbon support used, the following order of conversion values was observed: Pt (85–96%) $>$ Ru $\approx$ Ru/Pt (65–80%) $>$ PtRu (45–60%). Pt, Ru, and Ru/Pt catalysts supported on the same nanostructured carbon exhibited similar selectivities to COL. The similar performances of Ru and Ru/Pt catalysts confirm that for the Ru/Pt systems prepared by the two-step impregnation, Ru is deposited onto the Pt sites, and that there is no synergistic interaction between the metals on reaction. The PtRu systems, however, showed a notably improved selectivity (1.5–2 times higher than the corresponding monometallic catalysts supported on a given carbon support), suggesting a real synergistic effect between Ru and Pt. An electrophilic activation of the carbonyl group of CAL by electropositive Ru atoms associated with Pt (electron transfer from Ru to Pt) has been proposed to explain the synergy between these two metals in the case of AC supports [6].

In terms of supports, AC-supported catalysts present enhanced selectivities but poor conversions compared with the nanostructured carbon-supported systems. These results are essentially independent of the metal(s) impregnated, suggesting internal diffusion limitations to the transport of reactants along the microporous structure of the AC support. Indeed, XPS

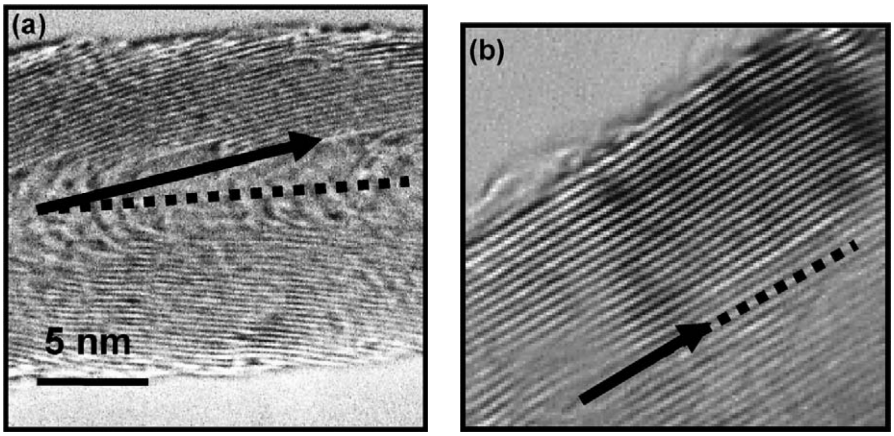
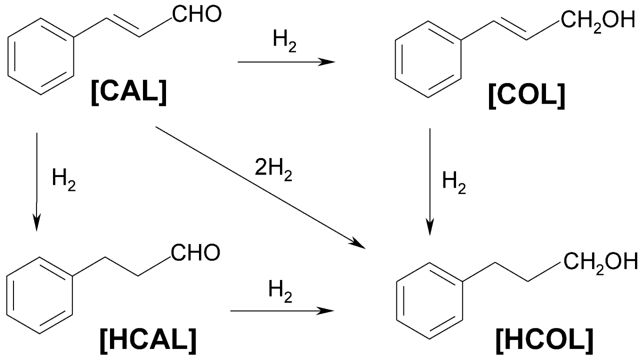


Fig. 1. HTEM micrographs of (a) GNF and (b) MWNT.



Scheme 1.

Table 1
CAL conversions (Conv.) and selectivity to COL (Selec.) obtained after 2 h of reaction over the different carbon supported catalysts

Support	2% Pt Conv./Selec. (%)[a]	2% Ru Conv./Selec. (%)	2% Pt 2% Ru Conv./Selec. (%)	2% Ru/2% Pt[b] Conv./Selec. (%)
SWNT	85/28	65/31	58/42 (**60/69**)	–
MWNT	95/32 (**97/66**)	66/35	44/55 (**79/93**)	80/22
GNF	96/14 (**90/15**)	78/18	60/29 (**92/17**)	76/21
AC	20/62 (**12/60**)	22/51	15/64 (**16/31**)	23/38

[a] The value in bold between parentheses correspond to the results obtained on heat treated samples.

[b] Catalyst mass 50 mg.

analyses performed on Pt systems suggested that on this latter support, most of the metal is localized in the porous network, because no Pt was detected on the catalyst surface, even at higher metal loadings. Therefore, it seems clear that for liquid-phase hydrogenation reactions, using mesoporous nanostructured carbon supports prevents significant mass transfer limitations, improving catalyst activity. It is assumed that the observed selectivity toward the unsaturated alcohol depends on the presence of sites on the catalyst surface that can activate the carbonyl group by allowing the easy supply of hydrogen. CAL may bind to the metal particles surface via the C=O group, the C=C group, or both [12]. Depending on the adsorption mode, the formation of COL or HCAL may be preferred. Bearing this in mind, and taking into consideration that high selectivity is obtained on AC regardless of the metal used, the better selectivity presented by the AC-supported catalysts can be explained by confinement effects in the slit-shaped pores of AC, where CAL can only enter sideways. A higher selectivity with increasing metal particle size, attributed to the lower probability of C=C bond activation compared with that of C=O bonds over larger particles, has also been reported [6]. Two explanations have been proposed for this effect: different adsorption modes onto the different planes of the metallic phase, the proportion of which varies with the particle size, and steric constraints between the phenyl group and the flat metal surface of a large particle. The good selectivity observed for Pt/AC-supported catalysts may then also result from the poorer metal dispersions obtained over this support. In the case of Ru and PtRu systems, the mean particle size does not increase significantly (PtRu/MWNT = 1.8 nm; PtRu/GNF = 1.5 nm; PtRu/MWNT = 2.4 nm). Finally, it has also been suggested that a zero-valent metallic surface is beneficial to the formation of unsaturated alcohols compared with a less reduced surface, and that the ratio Pt^0/Pt^{2+} has more influence on the selectivity to CAL than on the conversion values [6]. Hence, the poor selectivity measured on GNF-supported catalysts may be explained by the higher metal dispersions and the lower fraction of reduced metal determined for these catalysts (on GNF: Pt(0) = 62 at%, Pt(II) = 34 at%, Pt(IV) = 4 at%; on MWNT: Pt(0) = 82 at%, Pt(IV) = 18 at%). Thus, it appears that the use of AC allows only poor activity, due to internal mass transfer limitations, and fairly good selectivity due to either confinement effects or larger particle sizes. When nanostructured carbon supports are involved, higher activities are reached due to their mesoporosity, permitting good mass transfer, but poor selectivities are obtained, particularly for GNF, due to either smaller particle sizes or to the chemical state of the metal involved.

To overcome these latter limitations, we decided to perform high-temperature treatments on the catalysts, which should modify particle sizes as well as the concentration of surface functional groups on the support. The oxygen-containing surface groups of the carbon supports have been found to play a determinant role in anchoring the catalyst precursors as well as to affect catalytic performance [13–15]. The influence of the carbon surface chemistry on the hydrogenation of α,β-unsaturated aldehydes has been investigated, but contradictory results have been reported. In a study on crotonaldehyde hydrogenation over Pt/AC catalysts, Coloma et al. reported an increase in both activity and selectivity for C=O hydrogenation with an increase (up to 773 K) of the catalysts temperature of reduction [13]. De Jong et al. [14,15] reported that removal of oxygenated surface groups through an analogous thermal treatment (200–700 °C under inert atmosphere), significantly increases the activity of GNF-supported Pt and Ru catalysts but decreases the selectivity to COL. In our case, for Pt catalysts supported on GNF and AC, no significant changes were observed in catalytic activity after performing a thermal treatment under nitrogen at 700 °C for 2 h. For PtRu systems on GNF, we observed an increase in conversion and a decrease toward COL selectivity, together with an increase of selectivity toward HCOL. We found (by TEM) a PtRu mean particle size of 1.7 nm after heat treatment, pointing to good stability of this system. These results are similar to those reported by de Jong et al. [15] for Pt/GNF catalysts; thus we also can suggest that hydrogenation is facilitated by CAL adsorption on the carbon support after removal of the surface-oxygenated groups.

On activated carbon, heat treatment did not influence the conversion and led to a decrease in selectivity. TEM observations of the PtRu/AC systems before and after the heat treatment showed a significant increase in the mean particle size (from 2.4 to 4.5 nm), with a large particle size distribution (3–15 nm) for the heat-treated sample. This sintering phenomenon, which can induce pore-plugging, should affect the selectivity toward COL. Finally, for Pt and especially for PtRu catalysts supported on MWNT, these heat treatments led to an increase in both conversion and selectivity. A similar tendency was observed for the SWNT support. Noteworthy is the very high selectivity to COL (93%) obtained at high conversion level (80%) for the PtRu/MWNT system. For this latter catalyst, our TEM findings (Fig. 2) indicate that the increased selectivity was not limited to higher particle size distributions. Indeed, the mean particle size was not significantly affected by the high-temperature treatment (PtRu/MWNT = 1.8 nm; PtRu/MWNT treated at 700 °C under N_2 = 2.1 nm), revealing the high stability of these systems. In addition, no significant influence of the heat treatment on the chemical state of Pt was observed from XPS analysis. Thus, we propose that the greater conversions obtained after thermal treatment of PtRu/MWNT may be due to an effect of MWNT surface chemistry on CAL adsorption that aids the hydrogenation reaction. The role of carbon material surface chemistry on the adsorption of different aromatic compounds has been discussed previously [16,17], and we believe that on heat-treated MWNT samples, a π–π interaction between the CAL π electron ring and the basic π sites of the carbon nanotube surface may increase the CAL adsorption capacity. As far as the selectivity to COL is concerned, we propose that it can be associated with an electron transfer from the MWNT to the metal, which is enhanced by the removal of the electronegative oxygen atoms from the carbon surface. Indeed, electron transfer from the nanotube support to metal particles has already been reported [18], and the increase in electrical conductivity of carbon black with decreasing concentrations of surface-oxygenated functional groups is a well documented phenomenon [19]. This effect was particularly pronounced for MWNT-supported catalysts, because the mobility of the delocalized π-electrons is enhanced in the planes of such graphitic structures. As a matter of fact, we have measured conductivities of 9.1 and 6.2 S/cm for pellets of pure and HNO_3-treated MWNT, respectively. For GNF- and AC-supported catalysts, this effect tends to be less pronounced because of the orientation of the graphene layers and of hydrogen atoms at the external edges of their structures. The increase in electronic density around metallic particles promotes the adsorption and activation of CAL, also decreasing the probability of C=C bond coordination due to repulsion, thereby also increasing the selectivity toward unsaturated alcohol.

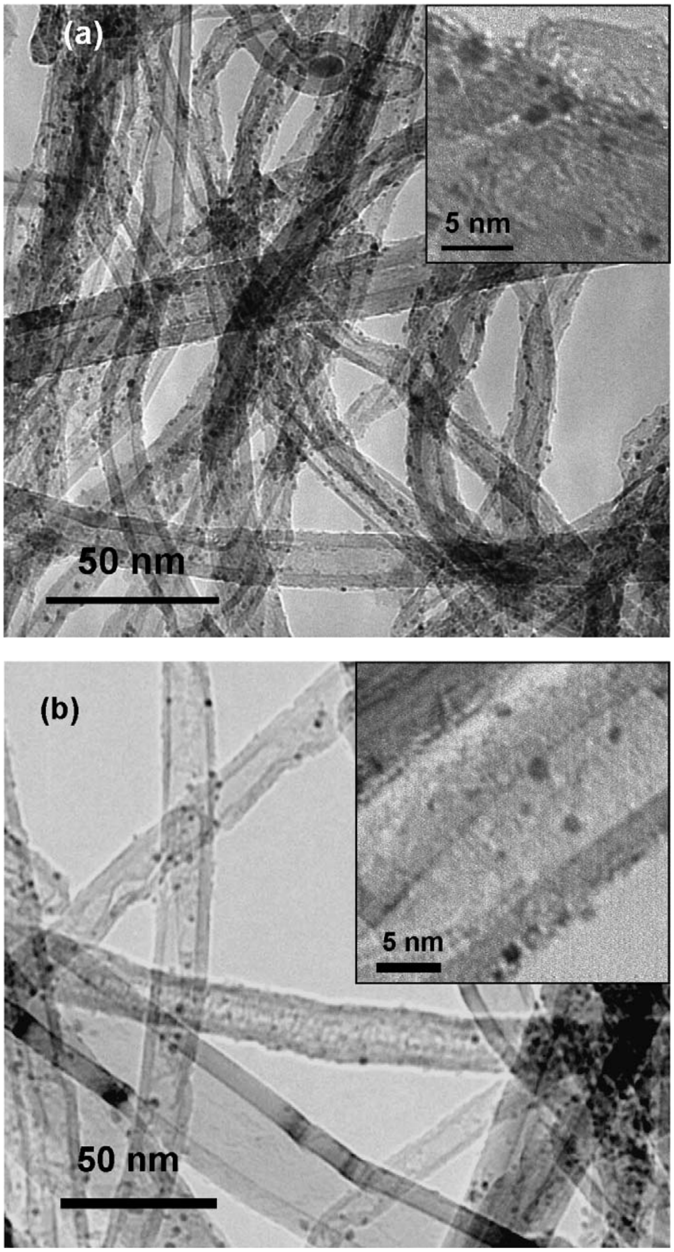


Fig. 2. TEM micrographs of (a) PtRu/MWNT reduced at 350 °C and (b) PtRu/MWNT reduced at 350 °C and heat treated at 700 °C under nitrogen.

4. Conclusion

We have developed very stable, active and selective catalysts for hydrogenation of CAL to COL under mild conditions. High activities are obtained by using MWNT, a mesoporous support that avoids, in contrast to AC, mass transfer limitations. The use of a platinum–ruthenium bimetallic system leads to higher selectivity than that obtained with monometallic systems. Finally, we have demonstrated that for MWNT-supported catalysts, high-temperature catalyst activation, which increases the electrical conductivity of the support without affecting the mean particle size of the metal, significantly promotes the selectivity toward COL, probably due to an electron transfer route from the MWNT to the metal.

Acknowledgments

H.V. gratefully acknowledges a research fellowship from the Agence Universitaire de la Francophonie, and R.P. acknowledges financial funding from ARKEMA.

References

[1] E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal. A: Gen. 173 (1998) 259.

[2] F. Rodríguez-Reinoso, Carbon 36 (1998) 159.

[3] M. Monthioux, P. Serp, E. Flahaut, C. Laurent, A. Peigney, M. Razafinimanana, W. Bacsa, J.-M. Broto, in: B. Bhushan (Ed.), Handbook of Nano-Technology, Springer, Berlin/Heidelberg, 2004, p. 39.

[4] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A: Gen. 253 (2003) 337.

[5] E.S. Steigerwalt, G.A. Deluga, C.M. Lukehart, J. Phys. Chem. B 106 (2002) 760.

[6] P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 40 (1998) 81.

[7] M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Kihn, P. Kalck, P. Serp, Chem. Eng. Sci. 58 (2003) 4475.

[8] R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic, J.-L. Duvail, Eur. J. Inorg. Chem. (2003) 610.

[9] F. Wen, H. Bönnemann, Appl. Organomet. Chem. 19 (2005) 94.

[10] K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, H. Nishiyama, J. Organomet. Chem. 272 (1984) 179.

[11] Y. Zhang, M.L. Toebes, A. van der Eerden, W.E. O'Grady, K.P. de Jong, D.C. Koningsberger, J. Phys. Chem. 108 (2004) 18509.

[12] R. Hirschl, F. Delbecq, P. Sautet, J. Hafner, J. Catal. 217 (2003) 354.

[13] F. Coloma, A. Sepúlveda-Escribano, J.L.G. Fierro, F. Rodríguez-Reinoso, Appl. Catal. A 150 (1997) 165.

[14] M.L. Toebes, F.F. Prinsloo, J.H. Bitter, A.J. van Dillen, K.P. de Jong, J. Catal. 214 (2003) 78.

[15] M.L. Toebes, Y. Zhang, J. Hájek, T.A. Nijhuis, J.H. Bitter, A.J. van Dillen, D.Y. Murzin, D.C. Koningsberger, J. Catal. 226 (2004) 215.

[16] T. Garcia, R. Murillo, D. Cazorla-Amoros, A.M. Mastral, A. Linares-Solano, Carbon 42 (2004) 1683.

[17] D.M. Nevskaia, E. Castillos-Lopez, A. Guerrero-Ruiz, V. Munoz, Carbon 42 (2004) 653.

[18] H.C. Choi, M. Shim, S. Bangsaruntip, H. Dai, J. Am. Chem. Soc. 124 (2002) 9058.

[19] D. Pantea, H. Darmstadt, S. Kaliaguine, L. Sümmchen, C. Roy, Carbon 39 (2001) 1147.