

Nanocarbons as Catalyst for Selective Oxidation of Acrolein to Acrylic Acid^[1]

B. Frank, R. Blume, A. Rinaldi, A. Trunschke, R. Schlögl

Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Abstract

Selective oxidations are key steps of industrial oil and gas processing for the synthesis of high-value chemicals. Mixed metal oxides based on redox active V or Mo are frequently used for oxidative C–H bond activation. However, multiple processes require precious metals or suffer from low product selectivity demanding an ongoing search for cost-effective alternatives. Recently, the nanostructured carbon was reported to catalyze the metal-free selective alkane activation by oxidative dehydrogenation (ODH). Electron-rich surface carbonyls coordinate this reaction and mimic the active oxygen species in metal oxide catalysts. Here we show that the graphitic carbon, beyond ODH, has the potential to selectively mediate the insertion of an oxygen atom into an organic molecule, i.e., acrolein. Multi-step atom rearrangements considerably exceed the mechanistic complexity of hydrogen abstraction and were so far believed to be the exclusive domain of metal (oxide) catalysis. In the carbon catalyzed process, the nucleophilic oxygen atoms terminating the graphite (0001) surface abstract the formyl hydrogen and the activated aldehyde gets oxidized by epoxide-type mobile oxygen, thus the sp^2 carbon acts as a bifunctional catalyst. Substantial similarities between the metal oxide- and carbon-catalyzed reactions could be identified. Our results shed light on a rarely known facet of applications of nanostructured carbon materials being decorated with diverse oxygen functionalities to coordinate complex catalytic processes. We could successfully transfer the results obtained from the graphite model to carbon nanotubes (CNTs) providing a higher surface area, defect density, and intrinsic activity, to substantially increase the reactivity per catalyst volume. Indeed, low dimensional nanostructured carbon is a highly flexible and robust material which can be modified in a multiple manner to optimize its properties with respect to the intended application. The exploration of fundamental similarities and differences in catalysis by metal (oxides) remains a significant challenge.

Introduction

In the past years, the application of nano-scaled carbons in catalysis has gained a lot of scientific interest due to the unique porous microstructure and the tuneable surface properties of this material [2-5]. In most cases the carbon structure is used only as a support for other catalytically active materials. Recent studies showed that oxygen functionalities ubiquitously present on the carbon surface have the potential to catalyze the ODH of ethylbenzene to form the important monomer styrene [6-8]. Among the great variety of different surface groups, the ketonic or quinoidic carbonyl groups are rich of electrons and thus possess the potential to coordinate this redox process. Hydrogen atoms can be abstracted from the hydrocarbon substrate forming surface hydroxyls, which in the following are reoxidized by gas phase oxygen [9]. In contrast to supported transition metal oxides, the nanocarbon as a simple platform is well adaptable to fundamental kinetic and mechanistic studies. However, multi-step atom rearrangements considerably exceed the mechanistic complexity of hydrogen abstraction and were so far believed to be the exclusive domain of metal (oxide) catalysis. The present study reports first results of a more general approach for using nanostructured carbon materials as heterogeneous catalysts for selective gas phase oxidation reactions [1]. In liquid phase under mild reaction conditions graphene oxide already

turned out to be an interesting catalyst for various types of organic reactions [10].

Acrylic acid (3.4 mio. tons world production in 2007 [11]) and its derivatives are important large scale products for the polymer industry [12]. The most common production process is the 2-step oxidation from propylene to acrolein followed by further oxygen insertion to form acrylic acid. The second step is usually catalyzed by mixed metal oxide catalyst based on Mo, V, and W. A yield of acrylic acid of > 95% is typically achieved at complete acrolein conversion [12] in the presence of up to 40% steam. Regarding carbon catalysis the low reaction temperatures of <300 °C would minimize the main drawback of using carbon materials as oxidation catalysts, as they inevitably combust in oxidative atmosphere at elevated temperatures [13]. The carbon catalyst as a completely innovative approach with promising first catalytic results is a candidate for deeper research. Carbon as the catalytic substance has significant advantages over the conventional metal-supported systems owing to the unique controllability of both its surface acidity/basicity and π -electron density through surface functionalization. We demonstrate a sustainable metal-free strategy for acrylic acid synthesis being free of the environmental burden of toxic transition metals.

Experimental

The catalytic reaction was performed in a fixed bed quartz reactor under atmospheric pressure and at 300 °C using sample amounts of 500 mg (100–300 μm). The feed comprising 5% $\text{C}_3\text{H}_4\text{O}$, 10% O_2 , 0–5% H_2O , and balance He was dosed by mass-flow controllers (O_2 , He) and saturators (H_2O , $\text{C}_3\text{H}_4\text{O}$) at a total flow of 25 ml min^{-1} (GHSV of 3000 h^{-1}). For kinetic measurements the temperature was varied between 275–325 °C using a feed comprising 2–10% $\text{C}_3\text{H}_4\text{O}$ and 5–20% O_2 balanced with He. Here, conversions below 5% were ensured by an increased total flow of 100 ml min^{-1} . Reaction components were quantified by an on-line gas chromatograph (Varian CP-4900).

HRTEM analyses were performed on a Philips CM 200 LaB6 microscope at 200 kV. Laser Raman spectroscopy was performed on powder samples by using an ISA LabRam instrument equipped with an Olympus BX40 microscope. The excitation wavelength was 632.8 nm and a spectral resolution of 0.9 cm^{-1} was used. Specific surface areas (BET) were determined by N_2 physisorption at –196 °C. For TPD the sample was subjected to a temperature ramp (10 K min^{-1}) in 25 ml min^{-1} of He. The molecules released from the surface up to 850 °C were quantified by an on-line mass spectrometer and an on-line gas chromatograph, respectively. Synchrotron-excited XPS analyses were performed at the ISSS beamline at BESSY II under quasi in-situ conditions in UHV at a temperature of 300 °C.

Results and Discussion

One of the most fascinating peculiarities of carbon catalysis is the possibility of a systematic study on the requirements of active sites for the target reaction. A huge amount of carbon allotropes is commercially available or can be easily prepared. Those tested in the oxidation of acrolein are listed in Tab. 1. These nanocarbons differ in their hybridization state, curvature and dimensions of stacks of basic structural units (BSU), as well as in the exposition of two types of surfaces, which strongly differ in their physico-chemical behavior, i.e., the basal plane and prismatic edges (Fig. 1). Structural and reactivity data was determined after 12 h time on stream. From the comparison of catalytic performances of the two types of graphites tested it is clear that the prismatic edges are most important for the catalytic reaction. More importantly, the poor performance of onion-like carbon (OLC) and fullerenes on the one hand and fishbone-type carbon nanofibers (CNF) on the other hand point out that both types of surfaces are crucial for selective oxidation of acrolein to acrylic acid. OLC and fullerenes are spherical nanocarbons, which solely expose the graphitic basal plane to the outer surface, whereas the here used variety of CNF selectively expose the prismatic edges to the outer surface, which is accessible to the gaseous reactants. The defective surface of commercial multiwalled CNTs (MWCNTs) appears to be the optimum compromise giving highest conversion and selectivity. Single shell nanocarbons such as fullerenes and carbon materials without long range order (activated carbon) vigorously combust under the applied reaction

conditions. The poor performance of the quinone catalyst MCT (macrocyclic trimer [14]), which is an excellent catalyst for ODH of ethylbenzene, suggests that quinones are not (exclusively) incorporated in the active site, which is confirmed by the relevance of the exposed basal plane being part of the active and selective catalyst. In this context it is coherent that sp^3 hybridized nanodiamond also shows a poor catalytic performance.

Table 1. Structural characteristics and catalytic performance of nanocarbon catalysts [1].

Sample	BSU characteristics	Predominantly exposed surface	S_{BET} / $m^2 g^{-1}$	$d^{[a]}$ / nm	X(C ₃ H ₄ O) / %	S(AA) / %
Natural graphite	planar, large, multilayer	basal plane	11.0	123	0.4	37
Synthetic graphite	planar, small, multilayer	basal plane / prismatic edges	349	6	8.8	66
MWCNT	curved, multilayer	basal plane, defects	541	9.9	14	85
CNF	curved, multilayer	prismatic edges	50	15–20	1.8	35
OLC	curved, multilayer	basal plane	315	5–15	4.5	75
Nano-diamond	-	sp^3 carbon	320	5–15	3	51
Fullerenes	strongly curved, monolayer	basal plane	1.7	0.7	31 ^[b]	41 ^[b]
MCT [14]	planar, small	quinone groups	5.0	-	5	12
Activated carbon	planar/curved, small, mono-/multilayer	basal plane, prismatic edges	835	-	26 ^[b]	51 ^[b]

[a] characteristic diameter of nanostructured carbon

[b] combustion of the carbon catalyst under reaction conditions

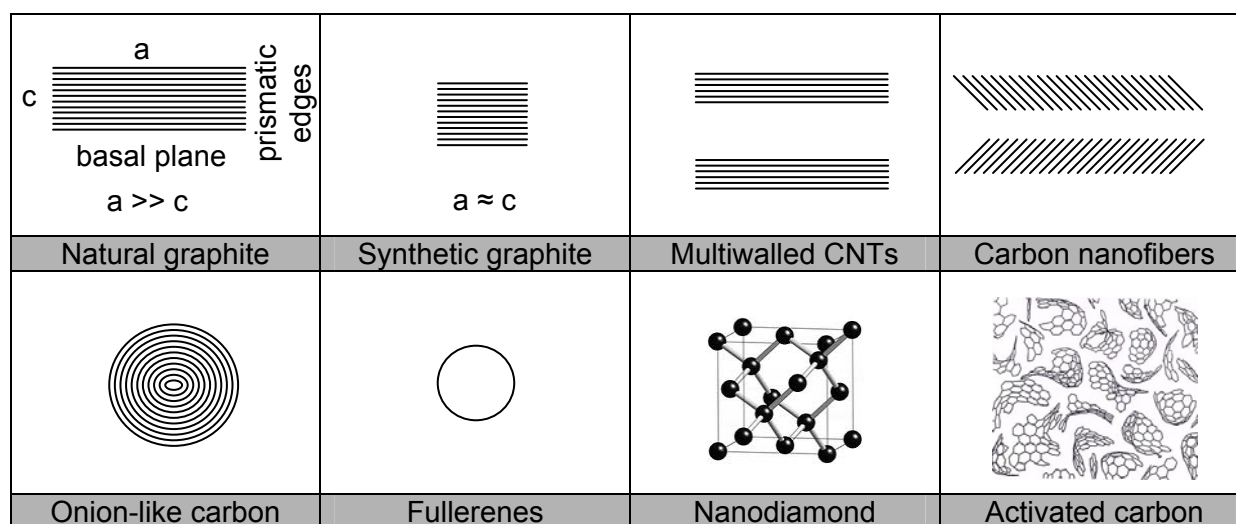


Figure 1. Illustration of structural assembly of nanocarbons (lines represent graphene layers).

The stability of catalytic performance of MWCNTs is shown in Fig. 2. The evolution of conversion and selectivity as well as the pronounced stability is observed for all the nanocarbon catalyst samples except for fullerenes and activated carbon, which steadily deactivate due to combustion. The initial reaction period is characterized by a decrease in activity accompanied by an increase in selectivity. This profile can be attributed to the initial loss of oxygen surface functionalities (mainly carboxyl groups, which were generated by MWCNTs purification procedure by HNO_3 washing) and the creation of the catalytically active surface as monitored by Raman spectroscopy. The decrease of the G-band relative to the D-band points at the *in-situ* defect formation on the outer surface of the MWCNT catalyst. After 12 h time on stream Raman spectra keep constant indicating that the catalyst structure is stable under reaction conditions. The structural integrity of the MWCNT catalyst is confirmed by HRTEM analysis of the 120 h used sample.

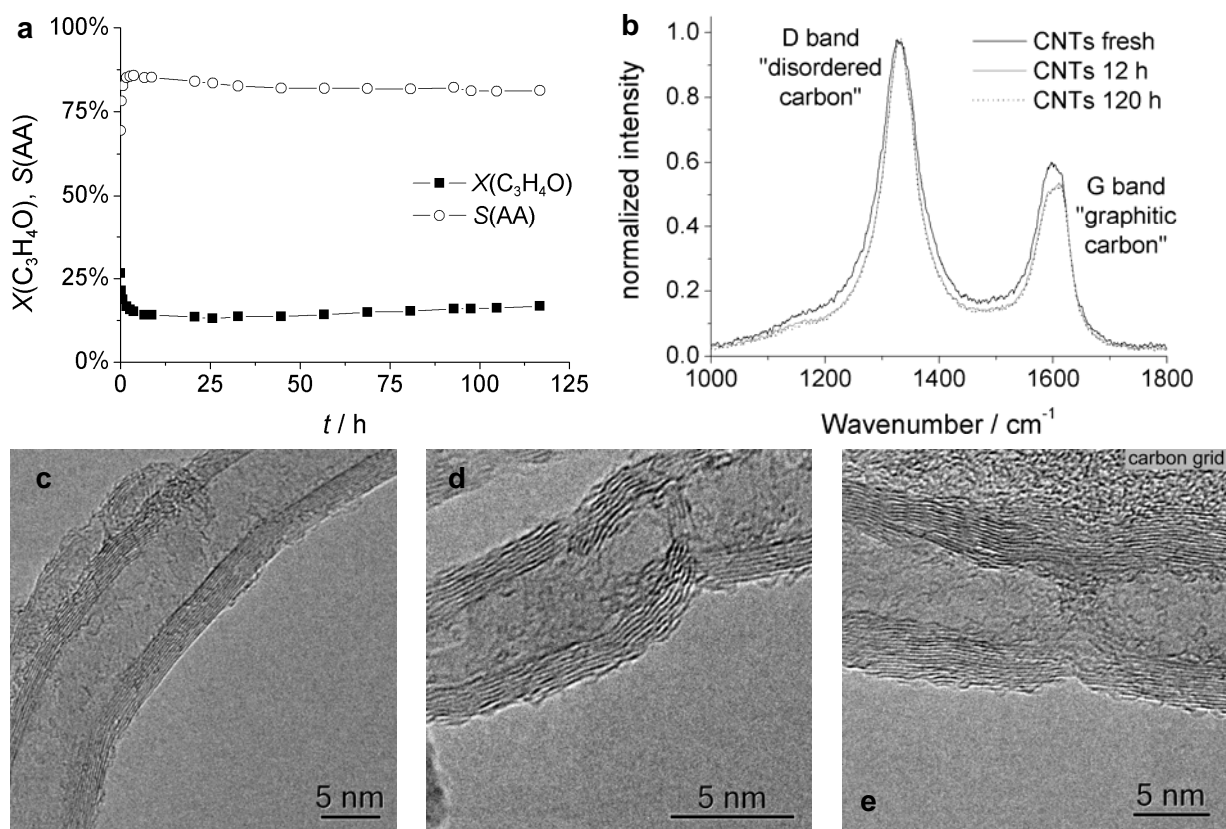
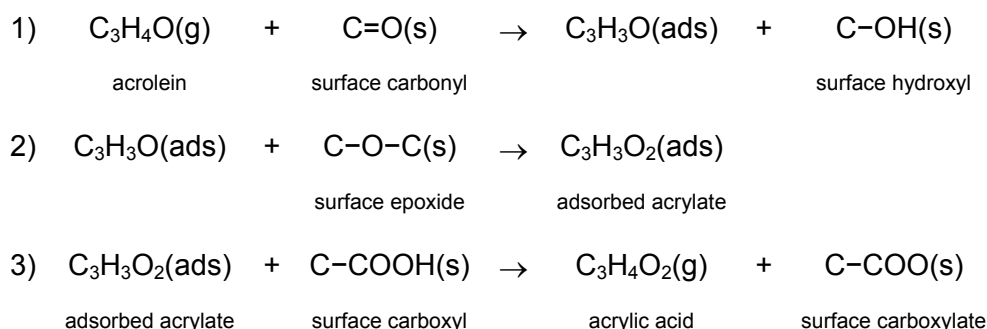


Figure 2. Stability of MWCNTs in the oxidation of acrolein; reaction conditions 5% $\text{C}_3\text{H}_4\text{O}$, 10% O_2 , balance He, 3000 h^{-1} , $300 \text{ }^\circ\text{C}$. (a) Catalytic performance, (b) Raman analyses of fresh and used catalysts, (c-e) HRTEM image of 120 h used catalyst [1].

The identification of the active site structure profits by previous mechanistic studies on acrolein oxide over V/Mo mixed metal oxides [11,15]. The two-step activation is initiated by the abstraction of the formyl hydrogen atom by nucleophilic oxygen species. The activated aldehyde gets subsequently oxidized by an electrophilic oxygen species, thus a bifunctional catalyst is required for selective formation of a strongly adsorbed acrylate anion. Protons from surface hydroxyls or from gas phase water molecules then enable the acrylic acid molecule to desorb from the catalyst surface [15]. In case of carbon catalysis the only nucleophilic oxygen surface group is the ketone or quinone carbonyl termination of the graphene layer. Its catalytic activity in H-abstraction is numerous described in ODH type reactions [8,9,14]. Thus it is plausible to assign the first step of acrolein activation to this type of surface functionality. For the second step a removable electrophilic oxygen species is required, preferably located on the basal plane of graphite. In previous studies on graphene oxide catalyzed selective oxidations in liquid phase, the selective conversion is accompanied by the loss of epoxide functionalities [16]. Furthermore, the removability of epoxide by

reduction with H_2 is predicted by theory [17]. Although an explicit experimental proof is missing, these observations could shed light on the reaction mechanism of gas phase oxidation of acrolein. The tentatively suggested active sites and reaction mechanism for this reaction over the graphitic carbon catalyst is given below.



Gas phase oxygen serves for the regeneration of active sites, i.e., reoxidation of surface hydroxyls to carbonyls and the continuous formation of epoxide oxygen by dissociative adsorption of O_2 on the basal plane of graphite. Charge localization induced by curvature of the graphene layer promotes the dissociation of strongly electrophilic dioxygen species such as peroxides, which are detrimental to the acrylic acid selectivity. In this way we can understand higher selectivities obtained for the MWCNTs as compared to the planar graphite catalysts. On the other hand, steam regenerates surface carboxyls or itself drives the desorption of acrylic acid to clean the catalyst surface [15].

The kinetic analysis of the reaction reveals an apparent activation energy of 85 kJ mol^{-1} , which decreases weakly in the presence of steam in the reaction feed mixture. The rate orders of O_2 and C_3H_4O over MWCNTs are 0.3 and 0.5, respectively, in agreement with the complex reaction mechanism suggested.

Following the industrial process conditions we added 5 vol.% H_2O to the reaction mixture to optimize the reaction conditions with regard to the yield of acrylic acid. For the MWCNTs the C_3H_4O conversion increases from 14% without addition of H_2O up to 19% in the presence of H_2O . In parallel, the AA selectivity also increases from 85 to 87%. A further increase of the steam content up to 40% drives C_3H_4O conversion and AA selectivity to 24% and 90%, respectively (Fig. 3a). The improvement of the catalytic performance is related to the modified surface properties of the carbon surface under wet conditions as suggested by a decreased activation energy of the reaction in the presence of steam. TPD analyses of the catalysts clearly reveal an increased amount of carboxyl species when switching from the dry to the wet feed, whereas the amount of other oxygen surface species remains fairly constant. A similar result is obtained by quasi in-situ XPS [1].

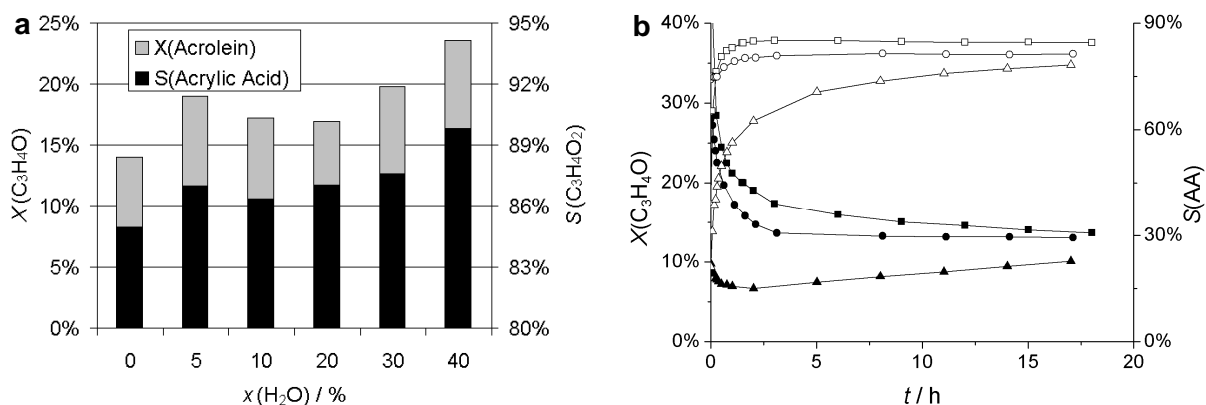


Figure 3. (a) Influence of steam addition on the catalytic performance of MWCNTs in the oxidation of acrolein, (b) Evolution of C_3H_4O conversion (full symbols) and acrylic acid selectivity (open symbols) over fresh HNO_3 treated MWCNTs (squares), after oxidation in air at $500 \text{ }^\circ\text{C}$ for 15 min (circles), and after calcination in He at $850 \text{ }^\circ\text{C}$ for 2 h (triangles) [1].

The high stability of the carbon catalyst is illustrated in Fig. 3b. It can be seen that the catalytic performance of the MWCNTs recovers within 1 day time on stream even after severe surface damage by oxidation in air at 500 °C for 15 min or by substantial defunctionalization of the surface by calcination in He at 850 °C for 2 h. This is a great advantage over traditional Mo/V based mixed oxides, which, if not held in optimum reaction conditions in terms of reaction temperature as well as O₂, C₃H₄O, or H₂O concentrations, irreversibly deactivate by phase transformation processes [18].

Conclusion

In conclusion, elemental carbon in the form of multiwalled carbon nanotubes was proven to be an active, selective, and highly robust catalyst for the oxidation of acrolein to acrylic acid. An acrylic acid productivity of 26.5 mmol g⁻¹ h⁻¹ was achieved, which is almost half as high as for the industrial doped MoV mixed oxide (about 60 mmol g⁻¹ h⁻¹) [12]. A certain potential for improvement of catalytic properties of the carbon catalyst can be expected as no attempts were made so far to optimize the catalyst with respect to stability at more common reaction temperatures or by doping the electronic structure of the carbon. Furthermore, the reaction mechanism of selective C₃H₄O oxidation could be clarified in substantial parts by highlighting the importance of nucleophilic and electrophilic oxygen species, the prismatic edges as well as the basal planes of graphite, and the abundance of protons being delivered either by carboxyl groups or by water.

References

- [1] B. Frank, R. Blume, A. Rinaldi, A. Trunschke, R. Schlögl, Oxygen insertion catalysis by sp² carbon, *Angew. Chem. Int. Ed.* (2011) in press. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.
- [2] P. Serp, J.L. Figueiredo, *Carbon Materials for Catalysis*, John Wiley & Sons, 2009.
- [3] B. Frank, J. Zhang, X. Liu, M. Morassutto, R. Schomäcker, R. Schlögl, D.S. Su, *Proc. DGMK Conf. „Production and Use of Light Olefins“* 163 (2009).
- [4] A.E. Lisovskii, C. Aharoni, *Catal. Rev. - Sci. Eng.* 36 25 (1994).
- [5] K.P. De Jong, J.W. Geus, *Catal. Rev. - Sci. Eng.* 42 481 (2000).
- [6] J. Zhang, D.S. Su, A. Zhang, D. Wang, R. Schlögl, C. Hébert, *Angew. Chem. Int. Ed.* 46 7319 (2007).
- [7] D.S. Su, N. Maksimova, J.J. Delgado, N. Keller, G. Mestl, M.J. Ledoux, R. Schlögl, *Catal. Today* 102-103 110 (2005).
- [8] M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, *Appl. Catal. A* 184 153 (1999).
- [9] J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, D.S. Su, *Science* 322 73 (2008).
- [10] D.R. Dreyer, C.W. Bielawski, *Chem. Sci.* 2 1233 (2011).
- [11] P. Kampe, L. Giebeler, D. Samuelis, J. Kunert, A. Drochner, F. Haaß, A.H. Adams, J. Ott, S. Endres, G. Schimanke, T. Buhrmester, M. Martin, H. Fuess, H. Vogel, *Phys. Chem. Chem. Phys.* 9 3577 (2007).
- [12] T. Ohara, T. Sato, N. Shimizu, G. Prescher, H. Schwind, O. Weiberg, K. Marten, H. Greim, in: *Wiley-VCH (Ed.), Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, 2003.
- [13] B. Frank, A. Rinaldi, R. Blume, R. Schlögl, D.S. Su, *Chem. Mater.* 22 4462 (2010).
- [14] J. Zhang, X. Wang, Q. Su, L. Zhi, A. Thomas, X. Feng, D.S. Su, R. Schlögl, K. Müllen, *J. Am. Chem. Soc.* 131 11296 (2009).
- [15] T.V. Andrushkevich, *Catal. Rev. - Sci. Eng.* 35 213 (1993).
- [16] D.R. Dreyer, H.-P. Jia, C.W. Bielawski, *Angew. Chem. Int. Ed.* 49 6813 (2010).
- [17] A. Jelea, F. Marinelli, Y. Ferro, A. Allouche, C. Brosset, *Carbon* 42 3189 (2004).
- [18] P.B. DeGroot, L.B. Levy, *J. Catal.* 76 393 (1982).