

Oxidative Dehydrogenation on Nanocarbon: Intrinsic Catalytic Activity and Structure–Function Relationships

Wei Qi, Wei Liu, Xiaoling Guo, Robert Schlögl, and Dangsheng Su*

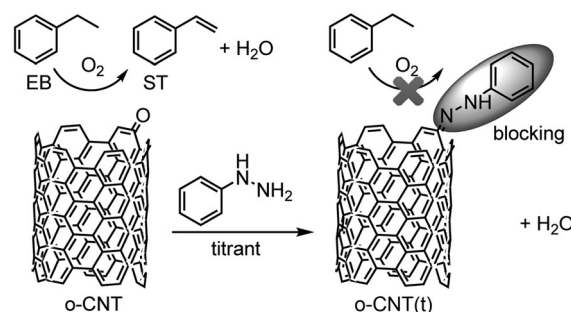
Abstract: Physical and chemical insights into the nature and quantity of the active sites and the intrinsic catalytic activity of nanocarbon materials in alkane oxidative dehydrogenation (ODH) reactions are reported using a novel *in situ* chemical titration process. A study on the structure–function relationship reveals that the active sites are identical both in nature and function on various nanocarbon catalysts. Additionally, the quantity of the active sites could be used as a metric to normalize the reaction rates, and thus to evaluate the intrinsic activity of nanocarbon catalysts. The morphology of the nanocarbon catalysts at the microscopic scale exhibits a minor influence on their intrinsic ODH catalytic activity. The number of active sites calculated from the titration process indicates the number of catalytic centers that are active (that is, working) under the reaction conditions.

Metal-free nanocarbon catalysts have attracted considerable research interest as a result of their significant advantages in terms of activity, stability, and regenerability.^[1–3] Significant efforts have been made in the design and fabrication of novel nanocarbon catalytic systems over the past decade.^[1] However, there are few quantitative studies on the intrinsic activity or detailed kinetics of carbon-catalyzed processes^[4] because of the surface complexity of the materials.^[5] The apparent activity of carbon catalysts are normally reported as reaction rates normalized by weight or surface area.^[4,6] As a result, it is difficult to compare the catalytic activity of various systems (carbon or other catalytic materials) fairly or to reproduce simply the synthetic or kinetic results from different research groups. In a theoretical or mechanistic sense, the measurements and kinetic studies based on turnover frequency (TOF) are more incisive than those made with specific or areal rates,^[6] and TOF is the parameter used to quantitatively describe the catalytic process at molecular level.^[7]

The difficulty in measuring the TOF for carbon catalysts is not only in determining the reaction rate but also in counting

the number of active sites, especially under reaction conditions. It is believed that surface oxygen functionalities (hydroxy, carboxylic acid, lactone, and ketonic carbonyl groups) on nanocarbons are the active sites for alkane oxidative dehydrogenation (ODH) reactions.^[8,9] However, identifying and quantifying these functionalities using current spectroscopy-based techniques, such as X-ray photoelectron spectroscopy (XPS) or temperature-programmed desorption (TPD), presents a significant challenge because of the similarities in molecular weight and physical/chemical properties between the different oxygen moieties.^[10–12] The chemical titration (passivation) method could provide the surface concentration of major oxygen functionalities on carbon nanotube (CNT) surfaces.^[13,14] However, the *ex situ* process cannot provide any information on the active sites under steady-state conditions and it also requires a series of samples and tedious steps, which is not practical for kinetic studies. To connect the chemical structure and quantity of the active sites to their steady-state intrinsic activity, we propose here an *in situ* titration technique as shown in Scheme 1. The direct measurement of the catalytic activity as a function of titrant consumption provides firm chemical evidence for the identity and quantity of ODH active sites on carbon catalysts. Information on the intrinsic catalytic activity obtained using this technique allows us to obtain an in-depth understanding on the nature of the carbon-catalyzed ODH process.

Figure S1 in the Supporting Information shows a schematic representation of the simple reaction unit used for the *in situ* titration process. The liquid-phase reactant ethylbenzene (EB) was introduced into the system with a peristaltic pump and was evaporated and premixed with oxygen and He in the vaporizer. The ODH reactions were performed under relatively gentle conditions (265 °C; EB conversion below 10%) to make sure that there was no significant structural damage, such as combustion or carbon deposition, to the



Scheme 1. Schematic representation of the *in situ* titration process for the ODH active sites on nanocarbon catalysts. o-CNT = oxidized CNT; o-CNT(t) = titrated o-CNT; ST = styrene.

[*] Dr. W. Qi, W. Liu, X. Guo, Prof. Dr. D. Su
Shenyang National Laboratory for Materials Science
Institute of Metal Research, Chinese Academy of Sciences
Shenyang, 110016 (China)
E-mail: dssu@imr.ac.cn

Prof. Dr. R. Schlögl
Fritz Haber Institute of the Max Planck Society
14195 Berlin (Germany)
and
Max Planck Institute for Chemical Energy Conversion
5470 Mülheim an der Ruhr (Germany)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201505818>.

carbon catalysts. The structural integrity of samples of both the fresh and used catalysts was confirmed by Raman spectroscopy, TEM, and N₂ adsorption measurements (Figure S2–S4). As shown in Figure 1a, the chemical titration on the oxidized carbon-nanotube (o-CNT) catalysts was performed under steady-state conditions. Phenyl hydrazine (PH) was chosen as the titrant because its molecular size, structure,

bonyl groups (C=O) on nanocarbons are identified as the active sites for ODH reactions. The selective removal (or poisoning) of the C=O active sites (that is, by reaction) is confirmed from the O and N 1s XPS and the ATR-IR (attenuated total reflectance IR) spectra (Figure S5–S8) of the fresh and the titrated o-CNT (denoted o-CNT(t)). These spectra clearly show that the intensity of the signals for the ketonic carbonyl oxygen species decreases and that the intensity of signals for the C=N group increases.^[12,14]

Based on the consumption of PH during the titration, the surface concentration of C=O active sites is around 0.7 C=O nm⁻², which is consistent with that calculated from an XPS element analysis for the increase of the nitrogen content after titration (0.8 C=O nm⁻²). It should be noted that this value indicates the surface concentration of active sites that are “working” under the given reaction conditions and it is not necessarily the same as the surface concentration of the ketonic carbonyl groups on fresh catalysts. First, some of the carbonyl functionalities are not accessible as a result of the porous structure of nanocarbons. Second, complex transformations occur between surface defects and various oxygen functionalities (such as hydroxys, carboxylic acids, and ethers) under ODH conditions.^[10] This is also the reason for the residual reactivity of the catalysts after titration as shown in Figure 1. The chemically active defects easily chemisorb oxygen and are oxidized under the reaction conditions.^[17] The newly formed ketonic carbonyl groups are responsible for the residual ODH activity after titration.

As shown in Figure 1b, the TOF for o-CNTs in ODH reactions (the slope of the line) is determined as 4.10×10^{-4} molecules of EB converted per C=O group per second, which is of the same order of magnitude as that obtained using other quantitative methods (such as TPD^[7,18] or ex situ titration^[14]). To our knowledge, the present research is the first example showing that the TOF for nanocarbon catalysts could be obtained from a single in situ test. In all other reports, a series of samples with similar chemical structures were required and multiple steps of ex situ measurements were necessary. The TOF value indicates the reactivity of a single ketonic carbonyl group on the nanocarbon catalyst, and the facile measurement strategy provides sufficient basis for a detailed kinetic study and to investigate structure–function relationships.

The in situ titration method (to measure the TOF value) was applied on five typical nanocarbon catalysts (graphene oxides (GOs), CNTs, and onion-like carbons (OLCs); see Figure 2). These catalysts exhibit different morphologies on the microscopic scale, and their key structural parameters are summarized in Table 1. Figure 3 shows that the EB conversion rate and the rates normalized by surface area and oxygen content exhibit erratic changes because of the variations in the identity and quantity of the oxygen species on different materials. In contrast, the TOF values (EB conversion rate per active site; Figure 3, triangles) are quite similar for all of the selected catalysts, suggesting that the chemical nature of the active sites (the ketonic carbonyl or quinone groups) on various nanocarbons are similar. The microscopic structure, for example the surface area, morphology, and curvature, exhibits a limited influence on their intrinsic activity, at least in this size range (where the diameter of the nanocarbon

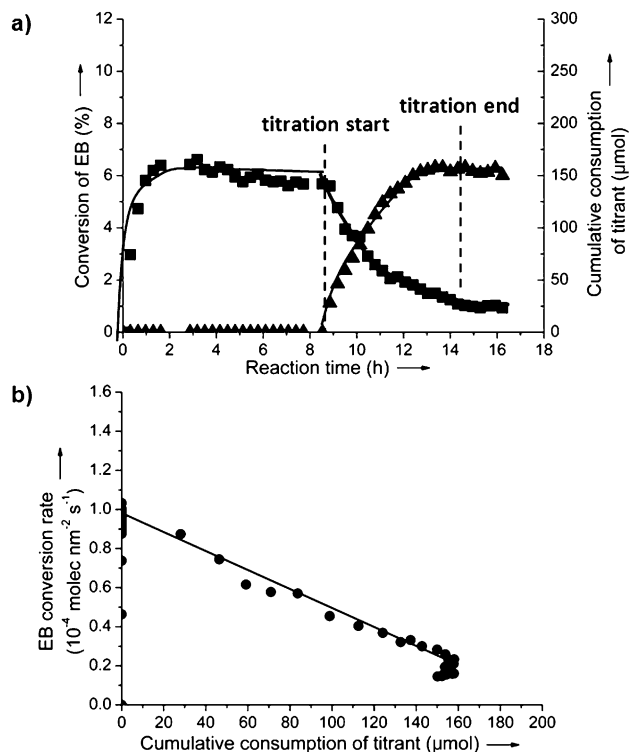


Figure 1. a) EB conversion (■) and titrant uptake (▲) as a function of time on stream during the steady-state activity measurement and in situ titration process. b) EB conversion rate as a function of the cumulative consumption of the titrant PH. Conditions: 538 K, 1.0 kPa EB, 2.0 kPa O₂, balance He, 200 mg catalyst.

and polarity are similar to that of EB. The similarities between the molecules allows PH to be used as an appropriate analogue to quantify the amount of active sites which could possibly be contacted by and react with EB.^[14] It has also been proven by independent control experiments that there are no side reactions between the titrant PH and reactants O₂ or EB under the chosen reaction conditions.

As shown in Figure 1a, the EB conversion rate (areal rate) dropped dramatically once the titrant PH has been introduced in situ (Figure 1a, titration start). The time at which complete depression of the catalytic activity occurred corresponded to the point at which the consumption of PH had reached saturation. Figure 1b shows that the EB conversion rate decreases monotonically with increasing PH uptake, and the linear dependence suggests that it is a site-by-site titration process. Considering the selective and stoichiometric reactions between PH and the ketonic carbonyl groups (forming hydrazones in more than 99.9% yield under relatively gentle reaction conditions),^[14–16] the ketonic car-

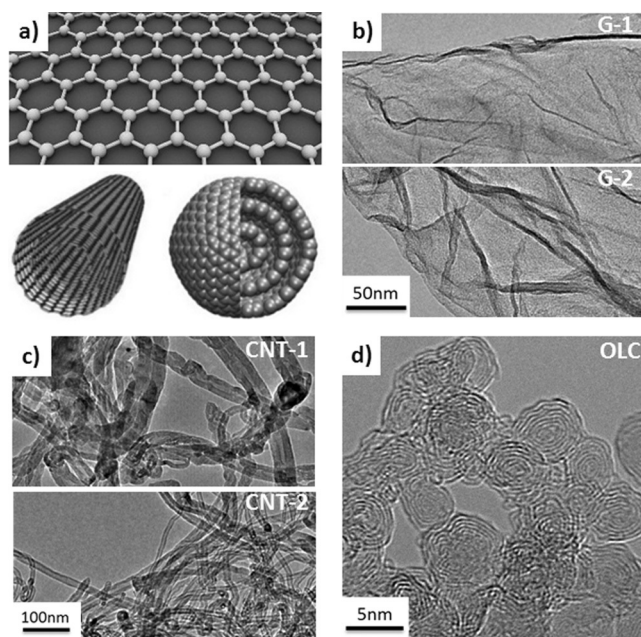


Figure 2. a) Schematic representations of the structures of the nanocarbon catalysts. b–d) TEM images of the catalysts employed, namely GO materials G-1 and G-2 (b), CNT catalysts CNT-1 and CNT-2 (c), and OLC (d), respectively.

Table 1: Key structural parameters for various nanocarbon catalysts.

Catalysts	G-1	G-2	CNT-1	CNT-2	OLC
shape	layers	layers	tube	tube	sphere
size (diameter)	μm	μm	70 nm	15 nm	5 nm
surface area ^[a]	546	449	192	219	263
C content [%]	82.3	82.8	96.2	94.4	90.2
O content [%]	15.4	13.8	2.32	5.01	7.4

[a] Surface area given in $\text{m}^2 \text{g}^{-1}$.

materials is above 5 nm).^[19] This observation is consistent with the theoretical estimations that the alternations of the chemical nature of the graphene layers caused by curvature is not so obvious when the diameter of nanocarbon is above 2 nm.^[20]

Another controversial issue that could be solved with the proposed titration technique is the variation in catalyst activity during the induction period in the carbon-catalyzed process. As shown in Figure 4, the OLC catalyst experiences a continuous drop of over 40% for the EB conversion (from 28% to 16%) in the first 6 h. The Raman, BET, TEM, and thermogravimetry/mass spectrometry (TG-MS; Figure S9–S12) measurements indicate that there is no obvious structural damage or carbon deposition on the used nanocarbon catalysts. The O 1s XPS analysis (Figure S13) reveals the difference in the distribution (identity and quantity) of the surface oxygen functionalities on the fresh and used OLC samples. The observed deactivation of the catalyst is indeed a result of the evolution of the surface functionalities on the catalysts, as clearly evidenced using the employed titration and TOF measurement strategy. It should be noted that the titration here needs to be performed ex situ to freeze (that is,

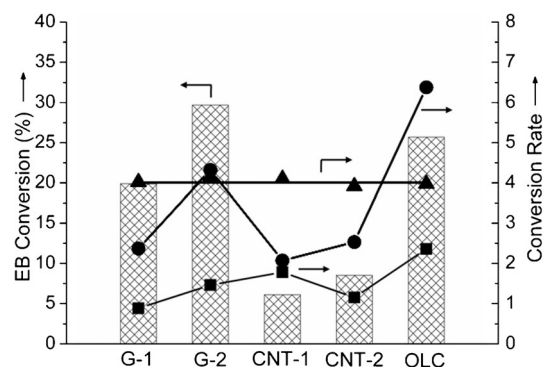


Figure 3. Comparisons of the ODH activity for various nanocarbon catalysts. EB conversion rate (bar) and conversion rates normalized by oxygen content (■; 10^{-7} molecules of EB converted per O atom per second), surface area (●; 10^{-4} molecules of EB converted per nm^2 per second) and number of active sites (TOF; ▲; 10^{-4} molecules of EB converted per ketonic carbonyl group per second), respectively. Conditions: 538 K, 2.8 kPa EB, 1.4 kPa O_2 , balance He, 100 mg catalyst.

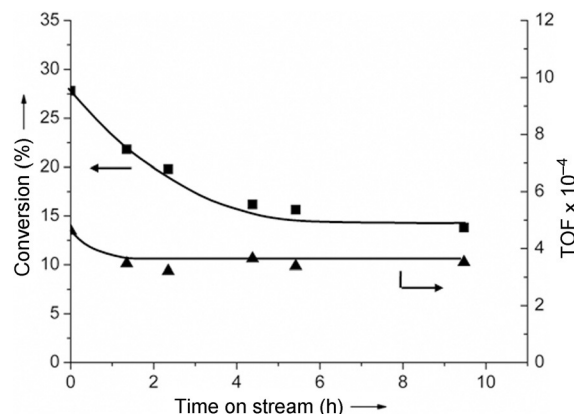


Figure 4. EB conversion (■) and TOF value (▲) for the OLC catalyst as a function of time on stream. TOF value is given as molecules of EB converted per carbonyl group per second. Conditions: 538 K, 2.8 kPa EB, 1.4 kPa O_2 , balance He, 100 mg OLC catalyst.

capture) the surface structure of the catalysts at various stages.^[14]

As shown in Figure 4, the plot showing the EB TOF values for the OLC catalyst does not exhibit the same shape as that for EB conversion as a function of reaction time. Based on the titration results, the concentration of the active sites on the OLC catalyst decreases under the given reaction conditions, which is consistent with the O 1s XPS measurements (Figure S13). Nanocarbon catalysts experience a rearrangement of the surface oxygen functionalities (transformation between surface defects and oxygen functionalities or transformation among different oxygen species), but the intrinsic activity actually does not change during this period. These results indicate that the good fit between the reaction conditions employed and the chemical structure of the catalysts could guarantee the optimal performance of the catalytic systems.^[5,6] The active-site titration analysis shows the evolution of the surface structure of the nanocarbon catalysts under the reaction conditions. These changes in

surface structure serve as a reminder that the steady-state activity should be correlated with the chemical structure of carbon catalysts under reaction conditions, highlighting the importance of the in situ analysis.

In conclusion, insights into the intrinsic activity of metal-free nanocarbon catalysts through the proposed titration process allow detailed studies of both the kinetics of the systems as well as the structure–function relationships. The linear dependence of the ODH reactivity on the consumption of titrant (PH) indicates that the ketonic carbonyl groups on nanocarbons are active sites for alkane ODH reactions. The EB TOF value is used as a reliable kinetic parameter to evaluate the intrinsic activity of nanocarbon catalysts. Studies on structure–function relationships suggest that the chemical nature of the active sites are identical on various nanocarbons, and that the microscopic structure has only limited influence on their intrinsic reactivity. Carbon catalysts undergo a rearrangement of their surface chemical structure under reaction conditions, but the intrinsic activity per active site does not change in this period. This research shows the importance of exploring the intrinsic activities of nanocarbon catalysts, which is fundamental in the field of carbon catalysis to carry out detailed kinetic studies and to fairly compare catalyst reactivities.

Experimental Section

Nanocarbon-catalyzed EB ODH process: EB ODH rates were measured on nanocarbon catalysts (0.1–0.2 g) at 538 K using a tubular quartz flow reactor with plug flow. Reactant mixtures contained EB (99.9%), O₂ (99.99%), and He (99.99%) at a typical gas flow rate of 6000 mL h^{−1} of gas per gram of catalyst employed.

Chemical titration of nanocarbon catalysts for EB ODH reactions: The in situ titration process was performed under the same conditions as ODH activity measurements, and during which only the syringe for the substrate EB is switched to the syringe with PH (the EB solution of PH at around 2 wt. %). The consumption of the titrant and the deactivation of the nanocarbon catalysts could be directly observed with GC. The ex situ titration process was performed in the liquid phase. The consumption of the titrant could be measured with UV/Vis spectra on the filtrate or XPS measurement on the titration derivatives.

Acknowledgements

The authors acknowledge financial support from the NSFC of China (21303226, 21133010, 21573256, 51221264, and 21261160487), the “Strategic Priority Research Program” of the Chinese Academy of Sciences (grant number XDA09030103). The authors acknowledge the kind supply of graphene oxide from Prof. Dr. Chengmeng Chen, Sino-carbon, Institute of Coal Chemistry, CAS.

Keywords: active sites · carbon materials · heterogeneous catalysis · kinetics · oxidative dehydrogenation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13682–13685
Angew. Chem. **2015**, *127*, 13886–13889

- [1] D. S. Su, J. Zhang, B. Frank, A. Thomas, X. Wang, J. Paraknowitsch, R. Schlögl, *ChemSusChem* **2010**, *3*, 169–180.
- [2] a) J. H. Bitter, *J. Mater. Chem.* **2010**, *20*, 7312–7321; b) D. S. Su, S. Perathoner, G. Centi, *Chem. Rev.* **2013**, *113*, 5782–5816.
- [3] a) R. Schlögl, *Adv. Catal.* **2013**, *56*, 103–185; b) D. Chen, A. Holmen, Z. Sui, X. Zhou, *Chin. J. Catal.* **2014**, *35*, 824–841.
- [4] J. Zhang, D. S. Su, A. Zhang, D. Wang, R. Schlögl, C. Hebert, *Angew. Chem. Int. Ed.* **2007**, *46*, 7319–7323; *Angew. Chem.* **2007**, *119*, 7460–7464.
- [5] W. Qi, D. S. Su, *ACS Catal.* **2014**, *4*, 3212–3218.
- [6] a) M. Boudart, *Chem. Rev.* **1995**, *95*, 661–666; b) R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *54*, 3465–3520; *Angew. Chem.* **2015**, *127*, 3531–3589.
- [7] M. F. R. Pereira, J. J. M. Orfao, J. L. Figueiredo, *Appl. Catal. A* **1999**, *184*, 153–160.
- [8] a) J. Marulanda, *Carbon Nanotubes*, InTech, Rijeka, **2010**; b) J. L. Figueiredo, M. F. R. Pereira, *Catal. Today* **2010**, *150*, 2–7; c) B. Frank, J. Zhang, R. Blume, R. Schlögl, D. S. Su, *Angew. Chem. Int. Ed.* **2009**, *48*, 6913–6917; *Angew. Chem.* **2009**, *121*, 7046–7051.
- [9] G. Dathar, Y. Tsai, K. Gierszal, Y. Xu, C. Liang, A. Rondinone, S. Overbury, V. Schwartz, *ChemSusChem* **2014**, *7*, 483–491.
- [10] R. Wang, X. Sun, B. Zhang, X. Sun, D. S. Su, *Chem. Eur. J.* **2014**, *20*, 6324–6331.
- [11] a) T. G. Ros, A. J. van Dillen, D. C. Koningsberger, *Chem. Eur. J.* **2002**, *8*, 1151–1162; b) W. Xia, D. Su, A. Birkner, L. Ruppel, Y. Wang, J. Qian, C. Liang, G. Marginean, W. Brandle, M. Muhler, *Chem. Mater.* **2005**, *17*, 5737–5742.
- [12] a) H. Boehm, *Carbon* **2002**, *40*, 145–149; b) L. Langley, D. Villanueva, D. Fairbrother, *Chem. Mater.* **2006**, *18*, 169–178; c) K. Wepasnick, B. Smith, J. Bitter, D. Fairbrother, *Anal. Bioanal. Chem.* **2010**, *396*, 1003–1014.
- [13] M. L. Toebes, J. van Heeswijk, J. H. Bitter, A. J. van Dillen, K. P. de Jong, *Carbon* **2004**, *42*, 307–315.
- [14] W. Qi, W. Liu, B. Zhang, X. Gu, X. Guo, D. S. Su, *Angew. Chem. Int. Ed.* **2013**, *52*, 14224–14228; *Angew. Chem.* **2013**, *125*, 14474–14478.
- [15] a) A. Setyan, J. Sauvina, M. Rossi, *Phys. Chem. Chem. Phys.* **2009**, *11*, 6205–6217; b) C. Larabi, E. Quadrelli, *Eur. J. Inorg. Chem.* **2012**, 3014–3022.
- [16] D. Applequist, H. Babad, *J. Org. Chem.* **1962**, *27*, 288–290.
- [17] a) C. G. Salzmänn, S. A. Llewellyn, G. Tobias, M. A. H. Ward, Y. Huh, M. L. H. Green, *Adv. Mater.* **2007**, *19*, 883–887; b) V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* **2008**, *46*, 833–840.
- [18] a) I. Pelecha, O. S. G. P. Soares, M. F. R. Pereira, J. L. Figueiredo, *Catal. Today* **2015**, *249*, 176–183; b) N. M. Sanchez, O. S. G. P. Soares, M. F. R. Pereira, M. J. S. Montero, J. L. Figueiredo, F. Salvador, *Appl. Catal. A* **2015**, *502*, 71–77.
- [19] H. Terrones, M. Terrones, *J. Phys. Chem. Solids* **1997**, *58*, 1789–1796.
- [20] D. Holec, M. A. Hartmann, F. D. Fischer, F. G. Rammerstorfer, P. H. Mayrhofer, O. Paris, *Phys. Rev. B* **2010**, *81*, 235403.

Received: June 26, 2015

Revised: August 16, 2015

Published online: September 21, 2015