**ODH @ CNTs – Metal-free Catalytic Alkane Activation**


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**Abstract**

The conversion of alkanes into higher valued olefins by oxidative dehydrogenation (ODH) using supported transition metal oxides is a topic of intense research, however, the yield of alkenes is still too low for industrial application. A completely innovative approach is the metal-free carbon mediated ODH catalysis, which is so far predominantly investigated on the substrate ethylbenzene. After surface modification, commercial multiwalled carbon nanotubes (CNTs) can be used as stable catalysts also for the activation of alkanes (C2–C4), enabling alkene yields comparable with supported vanadia catalysts but avoiding the use of toxic transition metal oxides.

**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. 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. 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 redoxy process. Similar to the Mars-van Krevelen mechanism, hydrogen atoms can be abstracted from the hydrocarbon substrate forming surface hydroxyls, which in the following can dehydrate and the produced vacancy will be reoxidized by gas phase oxygen. In contrast to supported transition metal oxides, the nanocarbon as a simple platform is well adaptable to fundamental kinetic and mechanistic studies.

For the polymer industry the large scale products ethylene (21.8 mio. tons in 2007, Europe) and propylene (15.7 mio. tons), but also butadiene (2.2 mio. tons) are even more interesting than the styrene monomer (4.4 mio. tons). The light olefins are usually produced via catalytic steam cracking of naphtha. The oxidative activation, namely dehydrogenation, of lower alkanes provides numerous advantages: (i) cheaper feedstock, (ii) no thermodynamic limitation, (iii) decoupling of ethylene and propylene production, (iv) less coking/catalyst deactivation, (v) lower reaction temperature and pressure, and (vi) exothermicity.

However, the crucial drawback is the insufficient alkene selectivity due to consecutive combustion of the activated reaction product. The only exception is the ethylbenzene molecule, whose dehydrogenation product styrene is less reactive than the substrate and thus a relatively high yield can be obtained in this reaction. Due to the weaker C–H bond in, e.g., propylene as compared to propane, the activation energy of ODH is in general higher than that of consecutive alkene combustion, but also adsorption properties due to the generated π-bond play a crucial role for alkene selectivity. Thus, the alkene selectivity of the ODH reaction network increases with increasing reaction temperature. Here is the main drawback for the application of carbon catalysts, as they inevitably combust in oxidative atmosphere at elevated temperatures.

Regarding the selectivity issue it must be mentioned that decades of intense research on metal oxide catalysts for alkane ODH could not bring up a catalytic system fulfilling the demands for industrial application. The carbon catalyst as a completely innovative approach with promising first catalytic results is an interesting 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 alkene synthesis being free of the environmental burden of toxic transition metals. The present article reviews the recent activities in the field of ODH catalysis by carbon materials at Fritz Haber Institute of the Max Planck Society, Berlin.
Table 1: Carbon materials tested in ODH catalysis

<table>
<thead>
<tr>
<th>Material description</th>
<th>Manufacturer</th>
<th>$S_{\text{BET}}$ / m$^2$ g$^{-1}$</th>
<th>$d$ / nm</th>
<th>ODH substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon black, lamp black</td>
<td>Degussa</td>
<td>26</td>
<td>-</td>
<td>ethylbenzene$^5$</td>
</tr>
<tr>
<td>high surface area graphite, HSAG 300</td>
<td>Timeal</td>
<td>267</td>
<td>-</td>
<td>ethylbenzene$^6$</td>
</tr>
<tr>
<td>multiwalled CNTs</td>
<td>Applied Science</td>
<td>26</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>onion-like carbon</td>
<td></td>
<td>456</td>
<td>5-10</td>
<td></td>
</tr>
<tr>
<td>nanodiamond$^1$</td>
<td>Beijing IT</td>
<td>245</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>multiwalled CNTs (long, thick-walled)</td>
<td>Tsinghua U</td>
<td>348</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>multiwalled CNTs (long, thin-walled)$^1$</td>
<td>Nanocyl</td>
<td>-</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>multiwalled CNTs (short, thin-walled)</td>
<td>Nanocyl</td>
<td>-</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>activated carbon, ROX 0.8</td>
<td>Norit</td>
<td>950</td>
<td>-</td>
<td>1-butene$^7$</td>
</tr>
<tr>
<td>multiwalled CNTs</td>
<td>Applied Science</td>
<td>42</td>
<td>50-200</td>
<td>n-butane$^8$, propane$^9$, ethane</td>
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<td>activated carbon$^1$</td>
<td>Alfa Aesar</td>
<td>837</td>
<td>-</td>
<td></td>
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<tr>
<td>activated carbon$^1$</td>
<td>COMBICAT</td>
<td>1081</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>multiwalled CNTs, NC 3100$^1$</td>
<td>Nanocyl</td>
<td>394</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>5 wt% B$_2$O$_3$ loaded CNTs, B-oCNTs</td>
<td>derivates of NC</td>
<td>262</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>5 wt% P$_2$O$_5$ loaded CNTs, P-oCNTs</td>
<td>3100</td>
<td>294</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

1) refluxed with nitric acid for purification and functionalization
$^1$) before use in catalysis

Experimental

Materials: The characteristics of commercial carbon samples inclusive specific surface areas $S_{\text{BET}}$, characteristic diameter $d$ and ODH substrate are listed in Tab. 1. Onion-like carbon was prepared by annealing of ultra-dispersed diamond. The sample NC 3100 was further surface-modified with 5 wt% B$_2$O$_3$ and P$_2$O$_5$ (B-oCNTs and P-oCNTs, where oCNTs are nitric acid treated ‘oxidized’ CNTs), respectively, by incipient wetness impregnation.

Catalyst characterization: Fresh and used samples were characterized extensively with bulk and surface sensitive methods. Details of each procedure are reported elsewhere.$^5$ The morphology of the samples was investigated by transmission and scanning electron microscopy (TEM and SEM), as well as by N$_2$ physisorption. Surface properties where determined by Raman, infrared, X-ray photoelectron spectroscopy (XPS), and electron-energy loss spectroscopy (EELS and ELNES), as well as thermogravimetric analysis (TGA-MS).

Catalytic testing: The ODH of hydrocarbons was performed in quartz tubular reactors at ambient pressure. The catalyst was held between two quartz wool plugs in the isothermal zone of a heating cartridge. Ethylbenzene was dosed via evaporation in flowing He, other gases were dosed by mass-flow controllers. Inlet and outlet gas compositions were determined by an on-line gas chromatograph. Details of catalytic testing are described elsewhere.$^5$ $^10$

For steady state isotope transient kinetic analysis (SSITKA) and periodic feed experiments 100 mg of sample were used with a flow rate of 10 ml$\text{min}^{-1}$ and aging period of 5 h in a C$_4$H$_8$/O$_2$/N$_2 = 1:1:4$ stream. The following gas mixtures were used: 2% $^{16}$O$_2$/He, 2% C$_4$H$_8$/He, 2% $^{16}$O$_2$/Ne, and 2% $^{18}$O$_2$/2% Ar/Ne.

High-pressure XPS: The in-situ XPS experiments were performed at beam line U49/2-PGM1 at BESSY, Berlin. The sample can be studied in the mbar pressure region due to a differentially pumped lens system. The detection limit is 0.1–1 atom% on the surface layer for most elements. The carbon surface during ODH reaction was investigated by using 20–25 mg of catalyst in a mixture containing butane and oxygen (1:1) at a total pressure of 0.25 mbar.$^8$

DFT calculations: A theoretical study was performed by using the CASTEP code to determine the 0 K reaction energies of step-wise dehydrogenation of butane to butenes and butadiene. The active sites were modelled by a supercell with carbonyl functional groups at zigzag edges of a graphite slab, which was cut perpendicularly to the basal plane and composed of six carbon atom rows.$^8$

Results and Discussion

Stability of carbon materials under ODH conditions, A critical aspect in the carbon-catalyzed ODH is the self-oxidation of the catalyst in the oxidative atmosphere. Figs. 1a and b compare the catalytic performances of various carbon catalysts in the ODH of ethylbenzene and propane, respectively.$^5$ $^6$ $^9$ A stable catalytic performance can only be achieved over carbons with long-range order, i.e. graphitic sp$^2$ or diamond-like sp$^3$ lattices. Disordered and amorphous
Fig. 1: (a) Stability of various carbons in the ODH of ethylbenzene (EB). --, ∇, 8: 20 mg, 10 ml min⁻¹, 2.16% EB, EB/O₂ = 1:1, 823 K; , ∇, ◦: as before, 790 K; 1, 7: 5 mg, 12.5 ml min⁻¹, 2.8% EB, EB/O₂ = 2:1, 723 K. (b) Stability of modified carbon nanotubes in the ODH of propane in comparison to an alumina-supported vanadia catalyst, 15 ml min⁻¹, C₃H₈/O₂/He = 1:1:48, 673 K; : 500 mg; , : 100 mg.

Fig. 2: Temperature-programmed desorption of (a) CO₂, and (b) CO from nitric acid treated CNTs after use in ODH and non-oxidative dehydrogenation of propane; (c) Temperature-programmed oxidation of used CNTs, B- and P-oCNTs, each with 5 wt% loading; (d) TEM image of B-oCNTs after use in ODH of propane.
mixtures of both, such as activated carbon or carbon black, rapidly deactivate by combustion within hours.

A distinct initial activation or deactivation period is typically observed. Depending on the reaction conditions, the steady-state performance is reached after 1–50 h. Here, a major restructuring of the carbon surface occurs: oxygen- rich carbons, e.g., after nitric acid treatment, usually show a loss of activity being accompanied by the thermal decomposition of carboxy groups and their anhydrides (Fig. 2a) and the formation of more stable (di)ketonic groups (Fig. 2b). In contrast, the high-temperature treated carbons with a low overall oxygen concentration usually increase in activity as the active sites are generated under ODH conditions. Against that, the Raman and microscopic characterizations reveal a high stability of the CNT structure being resistant to both the surface modification by heteroatoms and the ODH reaction conditions. The initial period is strongly influenced by the reaction conditions. Its duration decreases and the degree of steady-state surface functionalization increases with both the high temperature and the high oxygen concentration. ELNES analysis reveals that during the initial (de)activation period a defective layer comprising both sp² and sp³ hybridized carbon atoms is formed which is independent from the subsurface structure of the nanocarbon. In this viewpoint we can understand very similar kinetic constants such as activation energies (73 ± 5 kJ mol⁻¹), pre-exponential factors (1.5 ± 0.5 mmol g⁻¹ h⁻¹ kPa⁻¹) and rate orders of ethylbenzene (0.56 ± 0.10) and oxygen (0.32 ± 0.05) in the ODH of ethylbenzene over CNTs samples differing in length and wall thickness, as well as graphite or nanodiamond, altogether covering the carbon hybridization range from pure sp² via an intermediate state to pure sp³.

To achieve higher alkene selectivities at elevated reaction temperature, the chemical stability of carbon materials can be enhanced by modification with B₂O₃ or P₂O₅. Temperature-programmed oxidation reveals an increasing resistance against oxidation in the order CNTs< oCNTs< B₀CNTs< P₀CNTs (Fig. 2c). Both the onset temperature and the peak position shift to higher temperatures with increasing loading of the respective oxides. A positive impact of the modification on alkene selectivity is described below. Borate and phosphate block the combustion sites as a point of attack for O₂ adsorption. XPS and TEM show at least for B₂O₃, that the majority of this oxide is located in the cavity and on the ends of the CNTs (Fig. 2d). Only a minor fraction of the outer CNT surface is covered by an amorphous coating of 1–2 nm thickness, whereas a highly dispersed sub-monolayer of BO₃ species is expected to be omnipresent. A loss of the specific surface area (Tab. 1) indicates the filling of surface defects and holes in outer graphene layers.

Mechanistic insight into carbon-mediated catalysis: As implied by above TPD results and suggested by the widely accepted ODH reaction mechanism over metal oxide catalysts (Mars-van Krevelen), the surface oxygen groups play the key role in the carbon-mediated ODH. Using the ODH of propane as an example, the oxygen-free carbon is inactive for propane activation at temperatures below 600 °C. In the absence of oxygen in the gas phase, the oxidized carbon surface serves for the formation of a limited amount of propene and CO₂ corresponding to the amount of active surface oxygen atoms (Fig. 3a). Reoxidation of the catalyst occurs after combustion of a huge amount of propane adsorbed on the reduced surface. The carbon modification with B₂O₃ here drastically increases the propene selectivity by both, (i) a more selective substrate conversion and (ii) a reduced adsorption of propane on the reduced catalyst (irreversibly leading to CO₂ formation, Fig. 3b). As previously shown in Fig. 1b, the overall propene selectivity is here comparable to well-developed VO₂-Al₂O₃ catalysts.

Fig. 3: Periodic feed of (a) propane on the freshly oxidized 5 wt% B₂O₃-oCNTs, and (b) oxygen on the propane-reduced sample; 400°C.

The in-situ XPS analysis of the working catalyst gives further insight into the nature of carbon active sites. For instance, the OIs spectra of P₀CNTs during ODH of n-butane revealed two contributions at 531.2 ± 0.2 eV and 533.1 ± 0.2 eV, from C=O double bonds (ketones, anhydrides, lactones), and from C–O single bonds (ethers, hydroxyls, anhydrides, lactones), respectively. Under ODH conditions (n-C₄H₉O₂ = 1:1, 0.25 bar, 375 °C), the ratio of their intensities I(C=O)/I(C–O) is about 0.72, but sharply in
The consecutive dehydrogenation of the butenes to butadiene has lower barriers (0.25 and 0.40 eV, respectively) in agreement with the experimental observation of the predominant formation of butadiene in the high-conversion regime of the ODH of butane (see below). The C–H bond cleavage to be rate determining has been confirmed by isotope tracer experiment in the ODH of ethylbenzene. A distinct isotopic effect could be identified when switching the feed from C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{5} to the deuterium-labeled C\textsubscript{6}D\textsubscript{5}C\textsubscript{2}D\textsubscript{5} analogue (\(\gamma_{D}/\gamma_{D}=1.4\)).

**Substrates and selectivity:** The modified CNTs have been successfully tested in the ODH of ethylbenzene, 1-butene, n-butane, propane, and ethane. The investigations showed that the microstructure of the carbon material has minor impact on the kinetics and selectivity of the reaction, except for non-stable carbons with long-range disorder. For the ODH of ethylbenzene, due to the kinetic stability of conjugated electrons provided by the product styrene, the selectivity is usually as high as around 95% in the steady-state experiments depicted in Fig. 1a. The carbon catalysts under ODH conditions are even more active and selective than the typical multi-promoted iron catalyst used in the direct non-oxidative dehydrogenation processes so far, even at about 200 K lower reaction temperatures and without the addition of steam to the reactant mixture. 1-butene is another hydrocarbon substrate that can be subjected to moderately selective ODH without further catalyst modify...
cation. Similar to ethylbenzene, the reaction product butadiene has conjugated \( \pi \)-electrons providing a certain kinetic stability to suppress the consecutive combustion. Tab. 2 summarizes the catalytic performance at a total space-velocity of 0.2 kg h m\(^{-3} \) at 400 °C with 1.32 mol\% \( \text{O}_2 \).\(^7 \)

The selectivity of ODH over nanocarbons decreases drastically if the reaction product is not stabilized by conjugated \( \pi \)-electrons. For the lower alkanes (C2–C4), the selectivity is poor due to both the direct alkane combustion and the consecutive alkene combustion. One reason for this is the acidic carbon surface under oxidizing conditions. Electrophilic oxygen species being the intermediates of oxygen adsorption and carbon combustion, such as \( \text{O}_2^2^- \), O\(_2\), and \( \text{O}^- \), ultimately cause total oxidation, especially of the produced alkene providing an electron rich \( \pi \)-bond. The implementation of an electron-attracting dopant, such as boron or boron oxide reduces the generation of highly reactive oxygen species and is thus expected to increase the alkene yields. Indeed, the oxygen isotope exchange with the catalyst surface shows that the activation of oxygen is optimized (Fig. 6).\(^9 \)

The intermediates of isotopic scrambling on the unmodified CNTs likely bring on the high activity but poor selectivity to alkenes. On the contrary, the amount of mixed labeled oxygen almost vanishes on the B-dCNT sample, which is similar to the case of a \( \text{VO}_x\text{Al}_2\text{O}_5 \) catalyst being studied as a reference system due to its good performance in the ODH of propane.\(^10 \) The fact that oxygen activation on the modified CNTs gains impact on the overall reaction rate is nicely documented in the rate orders of the reactants in the ODH of ethane. For CNTs, B-CNTs and P-CNTs, the rate orders of ethane are similar at 0.60 \( \pm \) 0.05, respectively, whereas as the result of the surface modification the rate orders of oxygen strongly increase from 0.15 (CNTs) up to 0.40 \( \pm \) 0.05 (B- and P-CNTs).

The catalytic performance of the modified carbon catalysts in the ODH of \( n \) butane and propane was compared to differently supported vanadia catalysts by means of \( X-S \)-trajectories at given temperatures and feed composition (Fig. 7).\(^8,9 \) Clearly, the carbon catalysts hold a comparative and competitive performance to the established catalyst systems.\(^3,16,17 \) From Fig. 7b one can derive that the selectivity increases by heteroatom modification originating from the suppressed direct oxidation of the alkane. This is suggested by the extrapolated intercept near 100% propane selectivity at zero propane conversion as compared to the unmodified CNTs which have an intercept at approx. 20–50% selectivity.

Whereas for \( n \) butane a conversion of up to 40% could be realized in the given set-up at 400 °C, the activity for propane activation was somewhat lower and only 20% conversion could be achieved. This trend holds for ethane activation, which at 400 °C hardly exceeds 3% under comparable reaction conditions. The selectivity is about 40% for the unmodified and up to 75% for the B/P doped CNTs. The reduced reactivities go in parallel with the increasing deep oxidation stability of the alkanes with decreasing chain length.\(^18 \)

### Conclusions and Outlook

Nanocarbons have proven to be attractive alternatives to supported metal oxides in the ODH of light alkanes. The reaction mechanism via ketonic surface oxygen atoms substantially differs from the established model by Mars and van Krevelen for metal oxides as also documented by different activation energies.\(^9 \) On the carbon catalysts metal centers are not available and the redox process is coordinated solely by basic groups, which are

![Fig. 6: Oxygen exchange on the surface of (a) CNTs and (b) B-dCNTs along with switching the gas atmosphere from diluted \(^{16}\text{O}_2\) to \(^{18}\text{O}_2\) at 400 °C.](image-url)
absent on metal oxides. On the carbon catalysts the alkene yield can be drastically enhanced by the addition of heteroatoms such as boron or phosphorus oxides. This enables controlling the activation of oxygen on the molecular level which furthermore enhances the lifetime of the carbon catalyst in oxidative atmosphere. The major drawbacks are the reaction temperature being limited to 400–450 °C and, related to this, the inferior activity. The synthesis of highly active heterogeneous model catalysts, however, give rise to optimism to overcome this barrier.

Acknowledgement

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References


Fig. 8: Comparison of ODH performance of CNT catalysts with supported vanadia catalysts: (a) ODH of n-butane; \(^{16,17}\) (b) ODH of propane.\(^3\)