Transition metal loaded silicon carbide-derived carbons with enhanced catalytic properties

Lars Borchardt a, Frédéric Hasché c, Martin R. Lohe a,d, Martin Oschatz a, Franz Schmidt a, Emanuel Kockrick a,b, Christoph Ziegler e, Tristan Lescouet b, Alicja Bachmatiuk d, Bernd Büchner d, David Farrusseng b, Peter Strasser c, Stefan Kaskel a,∗

a Department of Inorganic Chemistry, Dresden University of Technology (TU-Dresden), Bergstrasse 66, 01062 Dresden, Germany
b Institut de Recherche sur la Catalyse et l’Environnement de Lyon (IRCELYON), University Lyon 1, CNRSC, 2, Av. Albert Einstein, 69626 Villeurbanne, France
c The Electrochemical Energy, Catalysis, and Materials Science Laboratory, Department of Chemistry, Chemical Engineering Division, Technical University Berlin, 10623 Berlin, Germany
d Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Institute for Solid State Research, Helmholtzstrasse 20, 01069 Dresden, Germany
e Department of Physical Chemistry, Dresden University of Technology (TU-Dresden), Bergstrasse 66b, 01062 Dresden, Germany

ABSTRACT

Carbide-derived carbons (CDC) with incorporated transition metal nanoparticles (~2.5 nm) were prepared using a microemulsion approach. Time-consuming post synthesis functionalization of the carbon support material can thus be avoided and nanoparticle sizes can be controlled by changing the microemulsion composition. This synthesis strategy is a technique for the preparation of highly porous carbon materials with a catalytically active component. In particular we investigated the integration of ruthenium, palladium, and platinum in a concentration ranging from 4.45 to 12 wt.%. It was found that the transition metal has a considerable influence on sorption properties of resulting nanoparticle-CDC composite materials. Depending on the used metal salt additive the surface area and the pore volume ranges from 1480 m²/g and 1.25 cm³/g for Pt to 2480 m²/g and 2.0 cm³/g for Ru doped carbons. Moreover, members of this material class show impressive properties as heterogeneous catalysts. The liquid phase oxidation of tetralin and the partial oxidation of methane were studied, and electrochemical applications were also investigated. Primarily Pt doped CDCs are highly active in the oxygen reduction reaction, which is of great importance in present day fuel cell research.

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1. Introduction

For many years micro- and mesoporous carbon materials have been in the special focus of scientific research. Particularly the outstanding adsorption properties combined with high chemical and hydrothermal stability [1–4] highlight the important role of this material class in the fields of hydrogen [5] and hydrocarbon energy storage, gas separation and purification, catalysis and electronics.

Nevertheless, most of the well known active carbon materials exhibit widely distributed irregularly curved pores with narrow bottle-necks [6] which turn out to be unsuitable for...
certain applications due to significant limitations in diffusion kinetics. Therefore the synthesis of mesoporous carbon materials have been studied extensively in the last decade [7–9]. Materials exhibiting narrowly distributed pore sizes are the ordered mesoporous carbons, synthesized from ordered mesoporous silica by exo-templating [10]. Depending on the template used, pore sizes can easily be adjusted. As one of the first Ryoo et al. have shown that such an ordered silica-templated carbon with a cubic pore geometry exhibits narrowly distributed pores of 3.1 nm diameter [9].

Another promising class of advanced carbon materials can be synthesized by the selective extraction of metal atoms out of metal carbides [11–15]. These carbide-derived carbons (CDC) also offer adjustable pore diameters as well as high specific surface areas (~2000 m²/g) and pore volumes (~0.64 cm³/g) [14–16]. Thus, CDCs are potential candidates as gas storage materials with outstanding hydrogen (~3 wt.%, 77 K, 1 bar) and hydrocarbon capacities (e.g. 16 wt.% methane, 298 K, 35 bar) [17]. Moreover these CDC materials are particularly discussed as electrode materials for super capacitor applications due to their large specific surface areas and high specific capacitances [16,18–20]. Especially hierarchically structured CDC materials containing micro- and mesopore systems have remarkable performances in supercapacitors. They exhibit specific capacitances of up to 170 F/g in organic and 200 F/g in aqueous electrolytes [21–24]. While the structure of the carbon material plays an important role, several studies have demonstrated that transition metal additives such as iron or ruthenium influence the structure and adsorption properties of the resulting CDC materials dramatically [25–30]. Moreover the addition of transition metals to carbon materials can also serve as a supplementary source for catalytic functionality.

In the following we present a strategy for the synthesis of silicon carbide-derived carbon materials containing nanoscaled, catalytically active transition metal particles based on polymeric precursors. Since post synthetic functionalization of carbon materials with catalytically active species often leads to sintering and agglomeration processes an in situ functionalization approach is described [31]. Thus the inverse microemulsion technique was used to form porous matrices with incorporated, highly dispersed metal compounds [31–33].

A microemulsion in general describes a ternary thermodynamic stable system of a non-polar oil phase, a surfactant and a polar phase. The inverse microemulsion in particular contains aqueous nanodroplets dispersed in an organic phase [34–35]. These nanodroplets serve as size-restrictive reactors for the growth of the nanoparticles. Thus the particle size of growing catalytic particles can be precisely tuned within a few nanometers by the molar water to surfactant ratio (R_w ratio) [33,36]. Incorporation of these particles is achieved by adding a polycarbosilane precursor to the organic phase, which finally polymerizes. These nanoparticle containing polycarbosilane composite materials were pyrolyzed in order to obtain silicon carbide, followed by silicon extraction by high temperature chlorination (Fig. 1). At the end of this process a highly porous carbon material with immobilized catalytically active nanoparticles is generated.

The aim of this paper is to introduce this new synthesis strategy for metal containing carbide-derived carbons. CDCs containing ruthenium, palladium and platinum have been prepared and possible applications for these materials have been studied. In this context the oxidation reaction of tetralin as well as the partial oxidation of methane have been tested as examples for both heterogeneous liquid and gas phase catalysis. Furthermore platinum doped CDCs were tested in the oxygen reduction reaction as an example for an application in electrochemistry. Depending on the used transition metal impressive performances in relevant catalytic reactions were achieved.

2. Experimental section

A scheme showing the steps for the preparation of metal doped CDC composites, comprising the preparation of metal containing polymeric PCS (M = Ru, Pd, Pt), ceramic SiC and carbonaceous CDC composites is given in Fig. 1. Detailed experimental procedures as well as information on characterization techniques are provided with the Supporting information part.

3. Results and discussion

3.1. Materials structure

Although the motivation of adding metal chlorides into a CDC synthesis was to create catalytically active species, remarkable influences on carbon microstructures and physisorption properties have also been noticed. While all metal/SiC composite materials are non-porous (S_b < 16 m²/g), the corresponding CDC materials exhibit high surface areas between 1500 and 2500 m²/g and pore volumes up to 2 cm³/g (Table 1).

Especially CDC-Ru exhibits a very high specific surface area (up to 2480 m²/g), and high micro- and total pore volume (up to 0.7 cm³/g and 2.0 cm³/g, respectively). The shape of this isotherm is type IV and the pore size distribution, calculated by QSDFT shows a hierarchical pore structure of micropores of approximately 0.9 nm and mesopores of 3.1 nm (inset Fig. 2). The hysteresis loop is seen at 0.4 < p/p_0 < 0.75 caused by the capillary condensation in the mesopores.

CDC-Pd and CDC-Pt also have high, but comparably lower surface areas and pore volumes (Table 1) which are similar to those of metal free bulk CDCs obtained from the same polymer-precursor (S_b = 1420 m²/g; v_micro = 0.56 cm³/g) [41]. The materials exhibit a hierarchical pore structure with micro- and mesopores of comparable size. It is known that many transition metals can serve as graphitization catalysts. Especially Fe, Co, Ni, Mn are known to catalyze the transformation of amorphous carbon into more ordered structures, but there are also some reports about the use of palladium as a graphitization catalyst [29]. Furthermore it is known that transition metal chlorides, like ruthenium chloride influence the chlorination process by increasing the etching rate [27,30]. Detailed information and Raman investigations about this topic are provided with Supporting information.

Elemental composition of the materials was investigated by energy dispersive X-ray spectroscopy (Table 2). All CDC materials contain silicon below the detection limit, so an effective silicon etching during the chlorination process can
be assumed. Furthermore oxygen content is lower than 0.5 wt.% for all composites. Compared to the theoretical value CDC materials contain the inserted metal in a decreased amount (metal content of 17 wt.% would be expected for the theoretical yield of 22%). On the one hand this is contributed to the fact that the surfactant used in the microemulsion approach also combusts into carbon partially, thus lowering the metal to carbon ratio in the final composite. On the other hand and maybe more importantly a generation of gaseous \(\text{MCl}_x\) species can explain the deficiency compared to the expected metal content.

To further characterize these nanoparticles transmission electron microscopy was carried out.

The microemulsion technique has found to be a useful approach for the size selective incorporation of metallic nanoparticles as reported recently\[32,33,35,37\].

**Fig. 3** shows TEM images of the well defined structured CDC-Pt (Fig. 3a and c), CDC-Pd (Fig. 3e) and CDC-Ru materials (Fig. 3f) compared with a commercial low-graphitized Pt/Vulcan XC 72R catalyst (Fig. 3b and d).

**Fig. 3a** and **b** clearly show significant differences in the carbon structure between a carbon black and the CDC supports. Carbon blacks display amorphous irregular conglomerates of carbon particles with diameters of about 50 nm. The network creates void spaces of 50 nm and more. The CDC support, in contrast, is characterized by a much denser and more regular structure with much smaller pore sizes. Surprisingly, the particle density in **Fig. 3c** appears to be higher compared to that in **Fig. 3d**, despite the much low-

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**Table 1 – Nitrogen physisorption data of silicon carbide-derived carbons with different metal additives.**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(S_g) (^{a}) ([\text{m}^2 \text{g}^{-1}])</th>
<th>(V_p, \text{total}^{b}) ([\text{cm}^3 \text{g}^{-1}])</th>
<th>(V_{p, \text{micro}}^{c}) ([\text{cm}^3 \text{g}^{-1}])</th>
<th>(V_{p, \text{meso}}) ([\text{cm}^3 \text{g}^{-1}])</th>
<th>(d_{\text{micropore}}) ([\text{nm}])</th>
<th>(d_{\text{mesopore}}) ([\text{nm}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC-Ru</td>
<td>2480</td>
<td>2.00</td>
<td>0.7</td>
<td>1.3</td>
<td>0.9</td>
<td>3.1</td>
</tr>
<tr>
<td>CDC-Pd</td>
<td>1540</td>
<td>1.35</td>
<td>0.5</td>
<td>0.85</td>
<td>0.9</td>
<td>3.1</td>
</tr>
<tr>
<td>CDC-Pt</td>
<td>1480</td>
<td>1.25</td>
<td>0.4</td>
<td>0.85</td>
<td>0.8</td>
<td>3.3</td>
</tr>
<tr>
<td>SiC-X (Ru, Pd, Pt)</td>
<td>&lt;16</td>
<td>&lt;0.01</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{a}\) \(S_g\) estimated at \(p/p_0 = 0.05-0.3\).

\(^{b}\) Total pore volume calculated at \(p/p_0 = 0.95\).

\(^{c}\) Micro pore volume calculated for pores \(d < 2 \text{ nm}\).

\(^{d}\) Pore diameter calculated by QSDFT methods for slit pores at 77 K using carbon kernel.
erPtloadings. Excellent uniform dispersion of platinum nanoparticles of $2.5 \pm 0.6$ nm size on the CDC support is shown in Fig. 3c. Electrochemical measurements and CO pulse chemisorptions have shown that these nanoparticles are catalytically accessible (further details are provided with Supporting Information).

Furthermore Foley et al. have reported that the electron rich graphene sheets in the carbon support interact with and thus stabilize the platinum nanoparticles [38].

Due to the low overall metal content of the samples and the small particle size of only a few nanometers, further TEM investigations were carried out on the samples to characterize the nature and composition of the incorporated metal nanoparticles. The particles were investigated by comparing lattice spacings determined from the TEM images with literature data, and local EDX measurements. It is known

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$m_{metal}$ [wt.%]</th>
<th>$m_{metal}$ [wt.%] theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC-Ru</td>
<td>7.0</td>
<td>17</td>
</tr>
<tr>
<td>CDC-Pd</td>
<td>6.5</td>
<td>17</td>
</tr>
<tr>
<td>CDC-Pt</td>
<td>12</td>
<td>17</td>
</tr>
<tr>
<td>CDC-Pt$_b$</td>
<td>4.45</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 3 – TEM image for CDC-Pt catalyst (a) 50 nm scale, (c) 10 nm scale, commercial Pt/Vulcan XC 72R catalyst (b) 50 nm scale, (d) 10 nm scale, CDC-Pd catalyst (e) 20 nm scale and CDC-Ru catalyst (f) 20 nm scale.
from literature, that palladium particles supported inside a ceramic SiC matrix will form palladium silicides at certain temperatures. Yoshimura et al. have shown that Pd/PdSi core-shell particles are formed due to the reaction of the metal particles and the surrounding SiC matrix at temperatures between 1173 K and 1373 K [39]. Additionally Lamber et al. reported on the formation of Pt, Si by heating platinum with a silica substrate under reducing atmosphere [40]. As it would be expected, the heat treatment combined with a high temperature chlorination of the materials also leads to the formation of silicides in some cases, possibly due to the reaction of gaseous SiCl4 with the metal nanoparticles. In the case of CDC-Pt materials Pt to Si ratios between 9:1 and 2:1 have been found using EDX analysis of single particles. For the CDC-Ru and CDC-Pd samples the silicon content is typically below 10%, and even Si-free particles can be found (for further details please see Supporting information).

3.2. Catalysis

3.2.1. Selective methane oxidation
The catalytic properties of ceramic and carbonaceous composites were tested in selective methane oxidation. In order to avoid oxidation of the porous carbon matrix, a low oxygen concentration was chosen. In the first step, methane is oxidized into carbon dioxide and water. In the following carbon monoxide and hydrogen can be formed using appropriate catalyst systems. In previous studies we have shown that the CeO2/Pt-CDC system is a promising catalyst for the selective methane oxidation. Furthermore we have shown that no carbon combustion of the CDC matrix was obtained [38]. However, the catalytic performances were strongly related on the nature of the porous matrix. In the present studies the influence of the transition metals were studied on the catalyst performance of silicon carbide (SiC-X) and carbide-derived carbon composites (CDC-X).

According to the methane conversions of different SiC-X and CDC-X composites the catalytic activity is strongly dependant on the applied metal sites and is presented in Fig. 4. Ruthenium (SiC-Ru), palladium (SiC-Pd) and platinum SiC-composite materials (SiC-Pt) offer significant activities. Methane conversions were obtained below 375 ºC for ruthenium, palladium and platinum ceramic composites. However in comparison to transition metal/CDC composites these ceramics show lower performances due to the low porosity and the resulting limited accessibility of active centers.

After chlorination, all CDC composites show considerable higher activities compared to the SiC intermediates (Fig. 4). The latter can be explained by significantly higher specific surface areas and pore volumes of CDC composites (Table 1). Ru-, Pd-, Pt-containing carbonaceous composites promote methane conversions up to 17% at 475 ºC for CDC-Pt. Additionally, only these composites promote reforming reactions explaining the higher methane conversions. The syn-gas production is strongly dependant on the applied transition metals since for palladium (CDC-Pd) and platinum systems (CDC-Pt) carbon monoxide and hydrogen can be already identified at significantly lower temperatures (250 ºC) compared to the ruthenium based system (CDC-Ru: 400 ºC). In agreement to previous studies, the hydrogen yield and carbon monoxide selectivity increases with higher reaction temperatures up to 12% and 42% at 475 ºC for the CDC-Pt catalyst, respectively [38]. Interestingly, the CO formation is shifted for the palladium based catalyst (CDC-Pd) to lower and hydrogen production to higher temperatures, respectively compared to the platinum system (CDC-Pt) (Fig. 4b). The latter suggests different reaction mechanisms for both catalyst systems. However, the corresponding ceramic SiC-Pd and SiC-Pt composites do not promote the syn-gas formation.

Additionally, no carbon oxidation of the CDC catalysts system were detected since the carbon balance as the molar ratio of all involved reactants and products remain constant in the studied temperature range. These results were confirmed by nitrogen physisorption measurements of fresh and used catalysts since similar specific surface areas, pore volumes and pore size distributions were obtained.

3.2.2. Catalytic tetralin oxidation
In comprehensive studies also the catalytic activity of carbonaceous CDC-X composites was tested in liquid phase tetralin oxidation. This reaction is widely used as a model reaction for industrial applications since the oxidation product 1-tetralone can be further used in diesel fuel additives and as a reactant for fine chemical applications. In contrast to literature reported procedures no additional aromatic or halogenated solvents were used. Additionally, pressurized molecular oxygen was used as oxidizing agent instead of more expensive peroxide species.

Similar as the methane oxidation discussed above, the tetralin oxidation is strongly dependant on the applied catalyst (Table 3). In contrast to the low activity for palladium systems (CDC-Pd), high tetralin conversions up to 28% and 44% were detected for the ruthenium (CDC-Ru) and platinum catalysts (CDC-Pt), respectively. This outstanding catalyst performance can be explained by the high activity of ruthenium and platinum species as oxidation catalyst in cyclohexene and tetraline oxidation. Furthermore the highly porous CDC matrix in combination with a hydrophobic surface leads to large hydrocarbon uptakes [24,41]. For all active composite materials similar selectivity of approximately 66% towards the formation of 1-tetralone was detected. Moreover, no additional by-products like naphthalene and 1-naphthalol were detected.

3.2.3. Oxygen reduction reaction (ORR)
The oxygen reduction reaction (ORR) is a sluggish, rate limiting reaction, which proceeds at the cathode side and therefore leads to significant cell potential and efficiency losses in hydrogen polymer electrolyte fuel cells (PEMFC).

A number of different catalyst concepts have emerged over the past years, which have shown promise to achieve the set Pt mass activity goals [42–49]; these include platinum monolayer catalysts, Pt skin catalysts, and alloyed Pt nanoparticle catalysts. Conventional carbon black supports and their graphitized variations continue to be the most popular catalyst support materials. However, innovative concepts for novel carbonaceous supports, on which Pt nanoparticles exhibit the benchmark mass and specific ORR activities of the carbon-black supported Pt particles have remained scarce. Studies comparing conventional carbon and carbon nanotube
supports [50] indicated that the support degradation plays a key role in the loss of the electrochemical active surface area of a cathode electrocatalyst at prolonged testing times [51–54]. Recently it was also shown that CDC materials exhibit superior performances as supports in direct methanol fuel cell applications (DMFC) [55].

The metal-doped CDCs described in this contribution offer high BET surface area, the possibility for controlled doping, high level of graphitization and structured frameworks. As such, it opens a promising prospect to achieve the long-term stability goals in fuel cell cathode catalyst research. Therefore platinum containing CDC-Ptb has been studied according its electrocatalytic activity for the oxygen reduction reaction. We find catalytic ORR activities comparable and superior to state of the art Pt/carbon catalysts involving conventional carbon supports, making CDCs a viable alternative catalyst support.

CDC-Ptb with a platinum loading of 4.45 wt.% were characterized with respect to their surface voltammetric behavior in supporting acid electrolyte as well as to their electrocatalytic reactivity for the oxygen reduction reaction (ORR) in acidic liquid electrolytes.

Fig. 5 (inset) shows the cyclic voltammetry (CV) profile for the CDC-Ptb catalyst. The CDC-Ptb catalyst exhibits a hydrogen absorption/desorption peak in the potential regime between 0.0 and 0.4 V vs. RHE, adjacent to a double layer capacitive current plateau starting at 0.4 V vs. RHE; anodically
thereof, the Pt hydroxide/oxide formation region is visible in the potential range of 0.7–1.0 V vs. RHE. The electrochemical active surface area (ECSA) of the supported Pt catalyst was estimated to 66 ± 4 m²/gPt and is consistent with literature values [56]. For ideal spherical, not contacting particles of 2.5 nm the theoretical specific surface area is 112 m²/g (Eq. (1)), thus this result highlights that the platinum nanoparticles on the mesoporous CDC support material are active and available for electrocatalysis.

$$S_g = \frac{A}{m} = \frac{6}{\rho \cdot d} \quad (1)$$

$S_g$ = specific surface area; $A$ = surface area; $m$ = mass; $\rho$ = density of the material; $d$ = diameter of the sphere.

Fig. 5 shows the oxygen reduction sweep voltammetry curves of CDC-Ptb catalyst at several rotating speeds. All measured polarization curves exhibit a plateau behavior in the potential regime between 0.06 and 0.60 V vs. RHE, where oxygen diffusion to the catalyst surface becomes the rate limiting process [57,58] and hence is sensitively dependent on rotation rate. At an anodic potential of about 0.70 V vs. RHE, the polarization curves exhibit a reactive regime dominated by mixed kinetic and diffusion control. Past 0.9 V vs. RHE, the voltammetric profile appears largely kinetically controlled, that is the surface catalysis is the slowest component in the overall reaction process, while mass transport is comparatively fast. This is why the sweeps become independent of the rotating speed. At the open circuit potential of about 0.96 V vs. RHE electrocatalytic conversion of oxygen ceases.

To extract the intrinsic catalytic activity, $j_{\text{kin}}$, of the CDC-Ptb ORR catalyst, the measured ORR current density, $j$, in Fig. 5 was corrected for mass transport according to

$$\frac{1}{j} = \frac{1}{j_{\text{kin}}} + \frac{1}{j_{\text{diff}}} \quad (2)$$

where $j_{\text{diff}}$ represents the diffusion limited ORR current density obtained from Fig. 5 at a given rotation rate. Table 4 reports the platinum mass and surface area based activity of the CDC-Ptb catalyst and a commercial Pt/Vulcan XC 72R catalyst [54]. Platinum electrochemical active surface area and particle size are reported in Table 4.

The CDC-Ptb catalyst exhibited a platinum based ORR mass activity, $j_{\text{mass}}$, of 0.19 ± 0.01 A mg⁻¹ Pt at 0.90 V vs. RHE and a platinum surface area based (specific) activity of $j_{\text{spec}}$, 283 ± 35 μA cm⁻² Pt at 0.90 V vs. RHE. Clearly, our CDC-Ptb catalyst with its low platinum loading and high BET surface area shows favorable ORR performance and is in line with reported [56] Pt mass and specific activities of commercial platinum catalysts supported on conventional Vulcan XC 72R or multi walled carbon nanotubes. Thus, our study suggests that CDC supports are viable fuel cell catalyst supports that are capable to realize the full activity of Pt nanoparticles at superior corrosion stability. Furthermore this material was compared to a post synthetic functionalized CDC derived by commercial SiC (Supporting informations).

In order to determine the number of transferred electrons during the oxygen reduction, we used the Koutecky–Levich equation [57,58] (Eq. (3))

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Table 4 – ORR catalyst performance.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$j_{\text{mass},0.9\text{V}(\text{RHE})}$ [A mg⁻¹ Pt]</th>
<th>$j_{\text{spec},0.9\text{V}(\text{RHE})}$ [μA cm⁻² Pt]</th>
<th>ECSA [m² g⁻¹ Pt]</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDC-Ptb</td>
<td>0.19 ± 0.01</td>
<td>283 ± 35</td>
<td>66 ± 4</td>
<td>2.5 ± 0.7</td>
</tr>
<tr>
<td>Pt/Vulcan XC 72R</td>
<td>0.15 ± 0.02</td>
<td>291 ± 40</td>
<td>53 ± 4</td>
<td>2.5 ± 0.6</td>
</tr>
</tbody>
</table>

Fig. 5 – Electrochemical characterization for CDC-Ptb catalyst, linear sweep voltammetry (LSV) with different rotating speeds performed anodically from 0.06 to 1.03 V vs. RHE with 5 mV s⁻¹ in oxygen saturated 0.1 M HClO₄ at room temperature (inset) cyclic voltammetry (CV) conducted from 0.06 to 1.00 V vs. RHE with 100 mV s⁻¹ in deaerated 0.1 M HClO₄ at room temperature.

Fig. 6 – Koutecky–Levich plot for CDC-Ptb at various potentials, data taken from Fig. 5.
1/j = 1/j_{\text{kin}} + 1/j_{\text{cat}} = 1/j_{\text{kin}} + 1/(B \cdot \omega^{1/2}) \tag{3}

B = 0.62 \cdot n \cdot F \cdot D(O_2)^{1/3} \cdot v^{-1/2} \cdot c(O_2) \tag{4}

Here, \( j \) is the current density, \( j_{\text{kin}} \) the kinetic current density, \( j_{\text{cat}} \) the diffusion limiting current density, \( \omega \) the rotating speed, \( F \) the Faraday constant (\( F = 96,485 \text{ C mol}^{-1} \)) and \( B \) is a parameter dependent on the experimental conditions. A theoretical value for \( B \) (Eq. (5)) of 0.467 mA cm\(^{-2}\) \( \cdot \text{s}^{1/2} \) was predicted for the four-electron oxygen reduction process published data for oxygen solubility (\( c(O_2) = 1.26 \times 10^{-3} \text{ mol l}^{-1} \)), oxygen diffusivity (\( D(O_2) = 1.93 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1} \)) and kinematic viscosity of electrolyte (\( \nu = 1.009 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1} \)). We then extracted the value of \( B \) specific to our experiments using a Koutecky-Levich plot for the CDC-Ptb catalyst at various potentials (Fig. 6).

The plot of \( 1/j \) vs. \( \omega^{-1/2} \) is linear and the fits run parallel, indicating a similar slope for various electrode potentials. The experimentally extracted mean \( B \) value for the various electrode potentials was 0.422 ± 0.003 mA cm\(^{-2}\) \( \cdot \text{s}^{1/2} \). The good agreement of the theoretical and experimental value of \( B \) corroborates the prevalence of the four electron over the two electron catalytic reduction pathway.

4. Conclusions

We have reported the synthesis of highly porous carbide-derived carbons with incorporated and highly dispersed nanoparticles. These materials were synthesized by using a microemulsion approach, followed by high temperature chlorination. Using this approach the nanoparticle species as well as their sizes can be controlled. Especially the incorporation of Pd, Pt and Ru salts was investigated here, showing that the chosen metal salts have eminent influence on the sorption properties of resulting carbide-derived carbons. In this context CDCs have been synthesized with specific surface areas of up to 2480 m\(^2\) g\(^{-1}\) and specific pore volumes of up to 2.0 cm\(^3\) g\(^{-1}\). Furthermore these composite materials show impressive properties in different catalytic applications. We have shown that Ru doped CDCs for instance, are efficient catalysts in the liquid phase tetralin oxidation. These materials show a tetralin conversion of 44%, and a selectivity of 66% after 6 h and 20 h. In addition, all CDCs (doped with either Ru, Pd or Pt) also show very good performance in the partial oxidation of methane. The conversion of methane already starts at very low temperatures (250 °C). At these temperatures also carbon monoxide and hydrogen were identified, due to reforming reactions, making these materials highly interesting as catalysts for the production of syn gas.

With respect to possible use as fuel cell materials, also the electrocatalytic performance of platinum doped CDC was tested. We have shown that this material is a promising alternative support material for fuel cell cathode catalysts. The observed Pt mass and specific activities, as well as the electrochemical active surface area are higher or comparable to those of commercial state-of-art Pt/carbon catalysts with conventional carbon black materials. The in situ incorporation of Pt nanoparticles into the carbon framework offer significant advantages for the long-term stability and corrosion resistance.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft, especially the priority program 1181 Nanomat for funding this work as well as Annette Wittebrock for laboratory supporting, Dipl.-Chem. Mehtap Oezaslan for inspiring discussion and the Zentraleinrichtung Elektronenmikroskopie at Technische Universität Berlin for TEM supporting. The Electrochemical Energy, Catalysis, and Materials Science Laboratory are a part of the Cluster of Excellence “Unifying Concepts in Catalysis” (UniCat) within the framework of the Excellence Initiative launched by the German Federal and State Governments, managed by the Technische Universität Berlin, Germany.

Author contributions: L.B. designed and performed the experiments, synthesized the materials and analyzed the data. M.O. helped with the experiments and analyses. M.R.L., A.B., B.B. were responsible for the TEM analysis. F.H. and P.S. were responsible for the electrochemistry part. T.L., E.K. and D.F. were responsible for the tetralin oxidation and partial methane oxidation. FS was responsible for the CO chemisorptions. C.Z. was responsible for the Raman measurement, S.K. supervised and coordinated the research. L.B., E.K. and M.R.L. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Appendix A. Supplementary data


References


