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Published in: Materials Today Energy

DOI: 10.1016/j.mtener.2024.101727

Published: 01/12/2024

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version: Suominen, M., Shi, J., Sainio, J., Hammouali, A., Moumaneix, L., Kobets, A., & Kallio, T. (2024). Effects of carbon support ozonation on the electrochemical reduction of CO₂ to formate and syngas in a flow cell on Pd nanostructures. *Materials Today Energy*, *46*, Article 101727. https://doi.org/10.1016/j.mtener.2024.101727

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Contents lists available at ScienceDirect

Materials Today Energy



journal homepage: www.journals.elsevier.com/materials-today-energy/

Effects of carbon support ozonation on the electrochemical reduction of CO₂ to formate and syngas in a flow cell on Pd nanostructures

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ARTICLE INFO

Pd

ABSTRACT

Keywords: Electrochemical reduction of CO2 Carbon support effect Carbon support ozonation

Pd convers electrochemically CO₂ into formate at the most positive known potentials but with low activity. Additionally, Pd is CO selective at more negative potentials, but is poisoned by the strongly bound CO* intermediate. Improving the activity and stability of Pd-based electrocatalysts holds promise for improving the electrochemical production of formic acid. Herein, we studied the effects of carbon support and its ozonation on the selectivity of electrochemical CO₂ reduction on Pd. The ozone treatment is found to improve the activity and formate selectivity at low overpotentials on single-walled carbon nanotube-supported catalysts with partial current densities up to -12 mA cm⁻² in 0.5 M KHCO₃ at potentials of -0.35 V and -0.45 V (vs. RHE). At more negative potentials, the catalysts become more selective towards CO and an opposite trend for CO-selectivity and ozonation duration is demonstrated. Unfortunately, the materials show deactivation in the form of decreased formate selectivity and increased hydrogen and CO evolution, especially when supports treated with ozone for a longer duration. The results and possible mechanisms are discussed based on previous findings and the physicochemical characterizations of the prepared catalysts. This work shows that a simple ozone treatment of carbons changes the efficiency of CO2 electroreduction.

1. Introduction

Production of formic acid by electrochemically reducing carbon dioxide (CO₂R) offers a viable route for closing the carbon cycle. Amongst the heterogeneous metal catalysts, the p-block metals In, Sn and Bi can reach close to 100 % formate selectivities when reducing CO₂ electrochemically. Unfortunately, such high selectivities are reached only at the cost of high overpotentials. Pd is generally known as a carbon monoxide (CO) selective CO₂R electrocatalyst, but also as a catalyst that can reach nearly 100 % formate selectivity at the most positive known potentials [1-4]. Thus, Pd offers means to reduce the required energy input for the electrochemical production of formic acid. However, Pd suffers from two issues: first, the currents where high formate selectivity (>80 %) is reached are low $(<5 \text{ mA cm}^{-2} \text{ in } 0.1 \text{ or } 0.5 \text{ M KHCO}_3)$ [5], and second, Pd actively poisons itself since the formed CO* intermediate binds strongly on its surface, further lowering its activity over time [2, 6]. In addition to being an interesting electrocatalyst for formic acid

production at more positive potentials than -0.4 V (vs. reversible hydrogen electrode (RHE)), syngas production on Pd-based electrocatalysts at more negative potentials (starting from -0.6 V vs. RHE) would be an interesting application, especially if high electrocatalytic activity could be reached with a low Pd loading.

Over the years, researchers have aimed to mitigate the issues of formic acid production on Pd with varying approaches. One such approach is alloying [1,7–10] or forming bimetallic catalysts with other metals that bind the CO* intermediate less strongly [11-16], thus preventing poisoning from taking place. Another approach is modifying the Pd crystalline facets to create ideal binding sites for the intermediates [17–19] or by aiming to form different core-shell nanoparticle structures for the same purpose [20-22]. Doping with heteroatoms, such as boron [23], has also been studied, as well as modifications with formate selective metal catalysts such as Bi [24]. Interestingly, similar approaches to those used to improve formate formation on Pd-based catalysts have also been applied to improve the selectivity and activity towards either

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https://doi.org/10.1016/j.mtener.2024.101727

Received 14 May 2024; Received in revised form 23 September 2024; Accepted 26 October 2024 Available online 29 October 2024

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CO or syngas formation [25-28].

Due to the scarcity and high price of Pd, its catalytic use requires finding means to lower its required amount, usually by supporting its nanostructures. Mainly Pd or its bimetallic, alloyed or core-shell particles with other metals have been supported on Vulcan carbon (VC) [1,2, 9,18-20,29-34], and very little research has been aimed at studying various supporting options or discussing the possible effects of the support in CO₂R selectivity. When pure Pd aerogel and commercial Pd supported on carbon were compared, the latter showed higher formate selectivity at low overpotentials [4]. Unfortunately, these aerogel materials were aimed at improving the CO selectivity and the changes in formate selectivity were not discussed from the carbon support point of view. A common approach in CO2R is nitrogen doping or functionalization of the carbon support which can enhance either CO [35] or formate production [36]. A bimetallic Sn-Pd aerogel showed improved formate formation after being supported on carbon nanotubes with NH₂ functional groups [13] because of improved adsorption of CO₂. On one occasion, a carbon-supported Pd nanoparticle catalyst was refluxed in glacial acetic acid [18], which revealed an improvement in formate formation. This was attributed to the highest tolerance of the refluxed electrocatalyst to CO poisoning. However, the analysis appeared to completely forget to examine the carbon support and only focused on the changes in the Pd.

Similarly, oxygen functionalities can be added into carbon supports, producing a myriad of effects in electrocatalysis – an approach that has received less attention in comparison to functionalizing with nitrogen. For example, ozonation of single-walled carbon nanotube (SWCNT) support enhanced hydrogen evolution while the loading of Pt could be reduced [37]. A similar approach could apply in aiming to reduce the loading of Pd for CO₂R electrocatalysts. Additionally, the mere improvement in hydrophilicity caused by oxygen functions on the supporting carbon may be interesting, since it is known that the reaction route from CO₂ to formate on Pd can take place via the reduction of HCO_3^- [11] or the electrochemical hydrogenation of CO₂ [38]. Thus, the interplay between hydrophobicity, usually needed when dealing with gaseous CO₂, and hydrophilicity, as our reactants are also in the liquid phase, becomes one key point to address.

To study the effects of oxygen-functionalized carbon supports in CO_2 reduction, we supported Pd nanostructures on two different carbon supports, VC and SWCNTs, and applied varying durations of ozone (O_3) treatment, *i.e.* 20 – 40 min, to incorporate different number of oxygen functional groups on the carbon supports. We studied the effects of the carbon support ozone treatment on formate formation in the low overpotential region (-0.25 to -0.45 V vs. RHE) as well as syngas formation in the high overpotential region (-0.85 to -0.95 V vs. RHE) on Pd using a neutral electrolyte (0.5 M KHCO₃) in a flow cell. The possible reaction mechanisms are discussed based on previous findings and known reduction routes. This work provides important information about the support effects and especially how hydrophilicity affects formate formation on Pd.

2. Materials and methods

2.1. Materials

All chemicals were used as received unless otherwise noted. Perfluorinated resin solution containing Nafion 1100W (5 wt%), hydrochloric acid (HCl) (32 %, EMSURE, Supelco), sulfuric acid (H₂SO₄) (0.5 M, Titripur, Supelco), hydrogen peroxide solution (H₂O₂) (contains inhibitor, 30 wt% in H₂O, ACS reagent) and potassium bicarbonate (KHCO₃) (ACS reagent, 99.7 %, powder, crystals) were purchased from Sigma-Aldrich. 2-propanol (CHROMASOLVTM, for HPLC, 99.9 %, Honeywell) and palladium(II) chloride (PdCl₂) (Premion, 99.999 % metals basis, Pd 59.5 % min) were purchased form Alfa Aesar. Ethanol (EtOH) (AA grade) was acquired from Altia Oyj. SH5 (5 % H₂ in Ar) and CO₂ gases (99.995 %) were purchased from Woikoski while N₂ was provided from an in-house line. VC (XC-72R) was acquired from Cabot and SWCNTs (TUBALLTM, <1 % metal impurities) were purchased from OCSiAl. The Nafion dispersion and 30 % H_2O_2 solution were stored in refrigerator while all other chemicals were stored under ambient conditions. Nafion 115 membranes were purchased from Ion Power and gas diffusion layers (GDL) (CT Carbon Cloth with MPL, W1S1011) were obtained from Fuel Cell Store. GDL were used as received while the Nafion membranes were pre-treated for 1h in boiling 5 % H_2O_2 solution, 30 min in boiling water, 1 h in boiling 0.5 M H_2SO_4 , and 3 times 30 min in boiling water. The pre-treated membranes were stored in deionized water. Deionized water (Milli-Q) was used in all experiments (18.2 M Ω cm at 25 °C).

2.2. Synthesis of supported Pd nanostructures

The PdCl₂ precursor solution was prepared by weighing approximately 100 mg of the salt into an Erlenmeyer to which 15 mL of EtOH was added. Under stirring, 10–20 drops of concentrated HCl (32%) were added and the solution was stirred for 1–2 h until opaque. Excess EtOH was then carefully evaporated using a water bath to reach a volume below 10 mL and the solution was then transferred to a volumetric flask to obtain a precise concentration.

The synthesis of carbon-supported Pd nanostructures followed a previously published route [37] with minor modifications. In short, a desired amount (30-60 mg) of carbon support material was weighed into a glass vial where O₃ treatment took place for either 20 min or 40 min using an O3 generator OZX-300ST from ENALY M&E Ltd. (maximum ozone output 200–500 mg h^{-1}). Non-treated supports were prepared following the same procedure. The support material was then carefully weighed into another glass vial where 2-propanol was added to reach a 4 mg mL^{-1} carbon support dispersion. The support was dispersed by 15 min of sonication using an ultrasound bath (Branson 3500) followed by 15 min of vigorous stirring. The required amount of PdCl₂ solution to reach the desired nominal Pd loading (5, 10, 15, 20 or 30 wt%) on support was then added to the carbon material dispersion over stirring, and the ultrasonication step was repeated before stirring the mixture for 3 days. The as-made mixture was then first dried using a rotavapor (120 rpm, 50 °C, <50 mbar), followed by 1 h in 80 °C air-circulated oven (Fratelli Galli). The reduction of Pd²⁺ to its metallic state was achieved by heating the samples to 300 °C (with the heating rate of 200 $\,^\circ\text{C}$ $h^{-1})$ under N_2 flow in a high temperature furnace (Nabertherm) and maintaining them at this temperature for 2 h under SH5 gas flow before allowing them to cool down under N₂ flow.

The catalysts are referred to in the text and figures with following abbreviations: Pd/VC-0 and Pd/SWCNT-0 (20 wt% Pd on pristine VC and SWCNTs, respectively), Pd/VC-20 and Pd/SWCNT-20 (20 wt% Pd on 20 min O_3 treated VC and SWCNTs, respectively), and Pd/VC-40 and Pd/SWCNT-40 (20 wt% Pd on 40 min O_3 treated VC and SWCNTs, respectively).

2.3. Electrochemical CO₂ reduction

The electrochemical reduction of CO₂ was performed using a custom flow cell presented in detail in our previously published work [39]. Ir mixed metal oxide (MMO) plate from ElectroCell served as counter electrode in the anode compartment, while leak-free LF-1.0-100 Ag/AgCl reference electrode from Innovative Instruments Inc. and GDL acted as the reference and working electrodes, respectively, in the cathode compartment. The potential of the leak-free reference electrode (Radiometer Analytical XR300 Reference Electrode). The GDL was prepared by spray painting a catalyst ink containing 1.5 mg mL⁻¹ catalyst (Pd + carbon support) and Nafion ionomer (ratio of 1:1 by weight to the catalyst) in 2-propanol. The ink was sprayed on an area of 2 cm \times 2 cm using a Badger model 100G airbrush. The loading of catalyst material (Pd + carbon support) was consistently 1.4 \pm 0.3 mg

cm⁻², determined by weighing the electrode before and after painting. A 0.5 M KHCO₃ aqueous solution served as both anolyte and catholyte and was circulated in the cell at 23 mL min⁻¹ using a peristaltic pump from Watson Marlow. A Nafion 115 membrane separated the two liquid compartments while the GDL separated the cathode and gas compartments. CO₂ was bubbled behind the GDL into the cathode compartment at 9–10 mL min⁻¹ and directed to analysis in micro gas chromatography (micro-GC) through the catholyte compartment and a rotameter.

Gaseous products were monitored online with an Agilent 990 micro-GC. The only gaseous products (H₂ and CO) were separated by a MoleSieve 5A column using Ar as carrier gas and detected and quantified using a thermal conductivity detector (TCD). The Faradaic efficiency of gaseous products (FE_{Gas}) was determined using the following formula

$$FE_{Gas} = \frac{i_{Gas}}{i_{Tot}} = \frac{z^* F^* \varphi_{Gas} * \nu_m}{i_{Tot}} * 100\%, \tag{1}$$

where i_{Gas} is the current used for generating a particular gaseous product (A), i_{Tot} is the total current used in bulk CO₂R at the time of GC sampling (A), z is the number of electrons transferred to produce a particular gaseous product (2 for both H₂ and CO), *F* is Faraday's constant (96485.33 C mol⁻¹), φ_{Gas} is the volume fraction of the gas product determined by GC, and ν_m is the molar flow rate of CO₂ gas determined with the rotameter (mol s⁻¹). The volume fraction of the gas was determined by periodically analyzing a calibration gas mixture from Woikoski with known contents of H₂ and CO and by comparing the peak areas of the analyte gas and the calibration gas.

Catholyte and anolyte were collected after CO₂R and the liquid products analyzed with a Waters 2690 HPLC equipped with a Waters 2414 refractive index detector. The only liquid product (formate) was separated by Aminex HPX-87H column (pH = 1–3, t = 65 °C, 5 mM H₂SO₄ eluent at 0.6 mL min⁻¹). The Faradaic efficiency of formate (FE_{HCOO}.) was determined using the following formula

$$FE_{HCOO-} = \frac{Q_{HCOO-}}{Q_{Tot}} = \frac{z^* F^* c_{HCOO-} * V}{i_{Tot} * t} * 100\%,$$
(2)

where Q_{HCOO} is the charge used for generating formate (C), Q_{Tot} is the total charge used in bulk CO₂R (C), *z* is the number of electrons transferred to produce formate (*z* = 2), *F* is Faraday's constant, c_{HCOO} is the concentration of formate determined by HPLC (mol L⁻¹), *V* is the volume of electrolyte, i_{Tot} is the total current used in bulk CO₂R (A) and *t* is the total time used for bulk CO₂R (s). The concentration of formate was determined by periodically analyzing a calibration solution with known content of formate and by comparing the peak areas of the analyte and the calibration solution.

 CO_2 reduction was performed by chronoamperometry (CA) for 1 h or 2 h at a time. A total of 4 h of CO_2R was performed in each applied potential (2 h + 2 h to collect liquid products in between). Electrochemical impedance spectra (EIS) were recorded between 20 kHz and 1 Hz at 10 mV amplitude before and after bulk CO_2R to determine solution resistance for *iR* correction. All potentials reported here have been corrected by the *iR* drop unless otherwise noted, and all potentials are reported against RHE, unless otherwise noted, and calculated according to the following formula

$$E_{iR free vs. RHE} = (E_{Applied vs. Ag/AgCl} - iR) + 0.2 + 0.059*pH,$$
(3)

where $E_{Applied vs. Ag/AgCl}$ is the applied potential (V), *i* is the current (A), and *R* is the solution resistance determined by EIS (Ω). The pH of the CO₂-saturated 0.5 M KHCO₃(aq) solution at room temperature (25 °C) was 7.6. All reported current densities have been normalized to the geometric electrode area unless otherwise noted.

2.4. Electrochemical analysis

The electrochemically active surface area (ECSA) of the materials was determined in 0.5 M $\rm H_2SO_4$ using a glassy carbon (GC) electrode. To prepare the working electrode, 2 mg of catalyst was dispersed into 1 mL of 2-propanol by 15 min of sonication, and 10 μL of the catalyst ink was applied on GC electrode (5 mm diameter) to reach a total mass loading of 0.02 mg on the electrode. After the catalyst ink had dried, 10 μL of Nafion solution (25 μL of 5 wt% Nafion solution in 1 mL of EtOH) was drop cast on top.

The cyclic voltammetry (CV) measurements were carried out using a rotating disc electrode at a rotation rate of 1600 rpm in N₂-saturated 0.5 M H₂SO₄ in a three-electrode cell configuration consisting of an asprepared working electrode, an iridium wire as a counter electrode and an Ag/AgCl saturated with 3 M KCl as a reference electrode. For *iR* correction, EIS was first recorded at open circuit potential (OCP) from 100 kHz to 0.1 Hz with 10 mV amplitude. After that, 5 consecutive CV scans were performed from -0.21 V to 1.00 V (*vs.* Ag/AgCl) at a scan rate of 50 mV s⁻¹. All potentials were converted to the RHE scale with the above formula (3).

ECSA was determined from the palladium oxide reduction peak observed in the CVs using the following formula

$$ECSA = \frac{Q_{PdO}}{\theta \cdot Q_{PdO,mono}},\tag{4}$$

where Q_{PdO} is the charge related to the palladium oxide reduction peak obtained by integration (μ C), $Q_{PdO, mono}$ is the charge value 405 μ C cm⁻² for PdO reduction, and θ is the surface coverage of oxygen [40]. Monoatomic layer of oxygen is assumed and thus the surface coverage was estimated to be 1 [40].

Linear sweep voltammograms (LSV) on Pd/SWCNT-0 and Pd/ SWCNT-40 were measured in 0.5 M KHCO₃ using a GC electrode (catalyst loading 0.2 mg cm⁻²) and a rotating disc electrode at a rotation rate of 1600 rpm. First, 30 min of N₂ was bubbled into the electrolyte followed by an LSV from -1.0 V to 0.75 V (*vs.* Ag/AgCl) at 5 mV s⁻¹. Then, 30 min of CO₂ was bubbled into the electrolyte, and increasing times of CO₂ reduction (5, 10, 20, 40 and 60 min) at -1.0 V (*vs.* Ag/AgCl) at 5 mV s⁻¹ was measured between each reduction step following [34].

2.5. Physico-chemical characterization

The crystal structure was characterized with X-ray diffraction (XRD) using Panalytical X'PERT PRO MPD Alpha 1 diffractometer and Cu K_{α} radiation ($\lambda = 0.15418$ nm, 45 kV, 40 mA) in a 20 range of 10°–90° with a scan step size of 0.0263°. The morphologies and particle size distributions were studied by transmission electron microscopy (TEM) on a JEOL JEM-2800 with an acceleration voltage of 200 kV. The samples were dispersed in ethanol (Etax AA, Anora, >99.5 wt-%) and then deposited on holey carbon grids (AGS147-3, Agar Scientific). Raman spectra were collected from films on GDL using Renishaw inVia™ Confocal Raman Microscope equipped with a 532 nm excitation laser, 830 l mm⁻¹ grating, and Charge Coupled Device (CCD) detector. Laser beam was focused on the sample using a 50x objective and the backscattered rays were collected at 180°. Contact angle measurements were performed on the films on GDL using Theta Flex optical tensiometer with 5 µL drop of the electrolyte (0.5 M KHCO₃). Thermogravimetric analysis (TGA) was performed on TA instruments TGA 5500 by heating a sample to 800 °C at 10 °C min⁻¹ rate under oxygen atmosphere. X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos Axis Ultra spectrometer with monochromated Al K_{α} -radiation, a pass energy of 40 eV, an X-ray power of 150 W and an analysis area of approximately 700 μ m \times 300 μ m. The binding energy scale is based on instrument calibration and no additional binding energy correction was applied. The elemental composition was determined from peak areas of highresolution core level spectra after Shirley background subtraction using equipment specific sensitivity factors.

3. Results and discussion

3.1. Material characterization

Before studying the effects of different carbon supports and the duration of ozone treatment on CO2 reduction, the Pd loading was optimized by synthesizing a series of electrocatalysts with nominal Pd loadings in the range of 5–30 wt% on SWCNTs with 40 min O₃ treatment and performing bulk CO_2R for 1 h at an applied potential of -0.45 V. The ozone treatment introduces increased number of oxygen functional groups, such as carbonyl and carboxyl groups, on the SWCNTs [37]. The FE_{HCOO-} increased and FE towards H₂ decreased as the nominal Pd loading was increased from 5 to 20 wt% (Fig. S1). Beyond 20 wt%, no further selectivity or activity enhancements is observed and, additionally, during synthesis, the Pd precursor salt dried on the glass vial walls indicating that all the Pd²⁺ cannot be effectively loaded on the SWCNTs. Therefore, the nominal Pd loading was fixed to 20 wt% for further experiments. TGA analysis indicated that the materials with different carbon supports have similar Pd loadings, close to the aimed 20 wt% (Table 1).

The morphologies of the Pd nanostructures were probed with TEM, and the results are shown in Fig. 1 and Figs. S2-3. All the materials exhibit spherical nanoparticles with an average diameter close to 3 nm, only Pd/VC-0 displaying a slightly larger average particle size (Fig. 1). In addition to these particles, the Pd/VC series exhibit much larger nanoparticles with diameters >10 nm, while Pd/SWCNT materials contain Pd nanowires (Fig. S2). The length of the nanowires would appear to shorten slightly with the ozonation duration, from 9.6 \pm 5.9 nm (0 min O_3) to 6.8 \pm 3.4 nm (40 min O_3), while their width is fairly similar between pristine (1.0 \pm 0.3 nm) and ozone treated SWCNTs (1.2 \pm 0.5 nm) (Fig. S3). We have previously observed the formation of nanowires on SWCNTs with Pt [37] and Pt-Ru [41] electrocatalysts. The morphology of the material with the highest formate selectivity (Pd/SWCNT-40) was also tested after CO2R and shows the retention of both nanoparticles and nanowires (Fig. S4). The average size of the nanoparticles seems to have been retained (3.4 \pm 2.1 nm) while the average length of the nanowires appears to have increased some (11 \pm 8 nm).

The crystal structure of Pd on all the studied supports matches that of metallic Pd (PDF#88–2335), both before (Fig. 2) and after (Fig. S5) CO₂R. After CO₂R, the SWCNTs-supported materials appear to have retained significant amounts of the electrolyte salt (KHCO₃), which becomes visible in the XRD patterns (Fig. S5a), despite thorough washing of the electrodes after CO₂R. The broad diffraction peak around 44° for Pd/VC-0 after CO₂ reduction can be attributed to the carbon support (Fig. S6).

Some clear differences between the materials are observed through their wetting behaviors (Table 1 and Fig. S7) and chemical structures (Raman spectra in Fig. 3). For Pd/SWCNTs, the contact angle decreases with the ozonation duration, *i.e.* from 118 \pm 5 (0 min O₃) to 89 \pm 4 (40 min O₃), while the ratio of D-band (1350 cm⁻¹) to G-band (1600 cm⁻¹) increases with ozonation duration, *i.e.* from 0.01 \pm 0.001 (0 min O₃) to 0.07 \pm 0.01 (40 min O₃). The former indicates that the hydrophilicity

Table 1

Results of Pd loading evaluated from TGA, the contact angle measurements, and ECSA evaluated from PdO reduction peak.

O ₃ duration/min	Pd loading/wt.%		Contact angle/ $^{\circ}$		$\rm ECSA/cm^2~mg_{Pd}^{-1}$	
	SWCNTs	VC	SWCNTs	VC	SWCNTs	VC
0	19.9	19.2	118 ± 5	130 ± 6	69.5	50.0
20	23.1	20.5	106 ± 2	129 ± 4	149.3	61.9
40	21.3	21.7	89 ± 4	131 ± 5	333.8	95.9

increases with increasing ozonation duration, while the latter suggests that surface defects increase with increasing ozonation duration. Both results are in line with the argument that longer ozonation treatment results in greater number of oxygen functional groups on the carbon [42]. The increasing amount of oxygen functional groups increases the hydrophilicity which can also improve mass transport in aqueous electrolytes, as discussed further in the next section. Neither contact angle nor Raman spectroscopy measurements show any significant changes for the Pd/VC materials indicating that the ozone treatment may have less of an effect on this carbon support. A more invasive acid refluxing method or an even longer ozonation treatment may be required to create a more significant number of oxygen functional groups on VC.

3.2. The effects of carbon and ozone treatment on CO_2 -to-formate electroreduction

The same nominal loading of 20 wt% Pd was applied on both SWCNTs and VC, and the influence of the duration of the ozone treatment on the samples' electrochemical properties was investigated. As is clearly indicated by the CVs and average CA results in Fig. 4a–b, the overall activity of the catalyst material increased as the ozonation treatment duration increases on SWCNTs. These findings are in good agreement with the differences discovered through contact angle analysis: increased wetting can result in increased mass transport to the active sites which could lead to higher current densities [37]. For the Pd/VC electrocatalysts, the change in activity with O_3 treatment duration is not as drastic as observed for Pd/SWCNTs according to the CVs (Fig. 4c), but the average total current density over 4 h of CO₂R more clearly indicates that the introduction of ozone treatment on VC also increases the activity in comparison to the pristine support material (Fig. 4d).

To find plausible explanations for the differences in activities, the electrochemically active surface areas (ECSA) were evaluated from palladium oxide reduction peak in an acidic media. The method lacks some accuracy but is considered a better alternative for Pd than the H₂ adsorption/desorption method [40]. The resulting CVs are depicted in Fig. S8 while the obtained ECSA values are gathered in Table 1. The charge associated with the reduction of PdO increases with increasing ozonation duration for Pd/SWCNTs, with ECSA values ranging from $69.5\ cm^2\,mg_{Pd}^{-1}$ (0 min O_3) to 149.3 $cm^2\,mg_{Pd}^{-1}$ (20 min O_3) and 333.8 cm^2 mg_{Pd}^{-1} (40 min O₃). In the case of the Pd/VC materials, a smaller increase in ECSA can be noticed with the increase in ozonation duration, from 50.0 cm² mg_{Pd}⁻¹ (0 min O₃) to 61.9 cm² mg_{Pd}⁻¹ (20 min O₃) and 95.9 cm² mg_{Pd}^{-1} (40 min O₃). Higher ECSA for longer ozonation duration could explain the increase in activity in both the Pd/SWCNTs and Pd/VC series. For the Pd/SWCNTs series, this observation could be attributed to improved wettability [37]. As discussed in the previous section, hydrophilicity and carbon defectiveness in the Pd/VC series do not increase with the increasing O₃ treatment duration. The increase in ECSA, therefore, could be due to slightly smaller Pd nanoparticle size with longer ozonation (Fig. 1a-b) or improved distribution of the nanoparticles. Any added defects, which may be outside the detection limit of our methods, can act as seed points for uniform growth of small nanoparticles.

Further, XPS was used to study the chemical composition of the samples supported on SWCNTs that had biggest differences between their overall activity (Pd/SWCNT-0 and Pd/SWCNT-40). Fig. S9 shows Pd 3d, O 1s and C 1s regions. Fig. S9a shows the Pd 3d region of both samples which look quite similar indicating that there is no electronic effect due to the ozonation that could explain the increased activity. Two components can be identified: a metallic peak with Pd $3d_{5/2}$ binding energy of 335.3 eV and another peak between 337 eV and 338 eV, which we tentatively assign to PdO [43]. The O 1s spectra of the samples are shown in Fig. S9b. The rather broad main peak can be explained with the presence of O=C bonds (~531 eV-532 eV) and O-C and/or OH-C bonds (~533 eV) [44]. The higher binding energy peak around 535 eV



Fig. 1. TEM images of (a) Pd/VC-0, (b) Pd/VC-40, (c) Pd/SWCNT-0, and (d) Pd/SWCNT-40.



Fig. 2. XRD patterns of 20 wt% Pd supported on (a) SWCNTs and (b) VC treated with O_3 for varying durations (0 min = black lines, 20 min = blue lines, 40 min = orange lines) before CO_2R .



Fig. 3. Intensity-normalized Raman spectra of 20 wt% Pd supported on (a) SWCNTs and (b) VC treated with O_3 for varying durations (0 min = black lines, 20 min = blue lines, 40 min = orange lines).

can be assigned to a Pd 3p peak. In Fig. S9c, the main C 1s peak at 284.5 eV can be assigned to sp_2 carbon. Additional features between 285.5 eV and 289 eV arise from different kinds of oxygen bonding [44] of which especially the C–O/C–OH related peak is prominent (around 286.5 eV). Also peaks at 292.5 eV and 295.9 eV are observed which can be assigned to K 2p but can also contain contributions from different fluorocarbons. Fig. S10 shows the F 1s spectra and survey spectra of the samples. The fluorine observed is related to the Nafion binder used. Atomic concentration based on XPS have been listed in Table S1.

A similar trend can be observed when looking at the selectivity towards formate at applied potentials of -0.35 V in Fig. 5 and Fig. S11 and at -0.45 V in Figs. S12–13. On Pd/SWCNTs, both the FE_{HCOO} and formate partial current density increase with increasing ozonation duration for both studied potentials. On the VC-supported materials, a small improvement of the formate selectivity can be attributed to the ozonated supports when compared to the pristine one. On both supports, the FE towards formate decreases as an increasingly negative potential is applied, as is known to happen on Pd electrocatalysts based on previous



Fig. 4. CVs of 20 wt% Pd supported on (a) SWCNTs and (c) VC treated with O_3 for varying durations, and 4 h average total current densities during CA of 20 wt% Pd supported on (b) SWCNTs and (d) VC treated with O_3 for varying durations (0 min = black lines, 20 min = blue lines, 40 min = orange lines). The CVs were recorded in 0.5 M KHCO₃(aq) electrolyte solution saturated with CO_2 at 50 mV s⁻¹, and they are noisy due to the use of gas fed flow cell in the measurements. CA was recorded for a total of 4 h at each applied potential in 0.5 M KHCO₃(aq) electrolyte solution saturated with CO_2 .



Fig. 5. FEs (a and c) and partial current densities (b and d) at an applied potential of -0.35 V in 0.5 M KHCO₃(aq) over initial 2 h of CO₂R on 20 wt% Pd supported on (a–b) SWCNTs and (c–d) VC treated with O₃ for varying durations.

findings [3,8]. The FE_{HCOO}. on both Pd/VC-40 and Pd/SWCNT-40 catalysts improves at a more positive applied potential (-0.25 V) (Fig. S14). However, the overall current density of the Pd/SWCNT-40 catalyst decreases to such an extent that the formate partial current density suffers a 50 % decrease in comparison to -0.35 (Fig. 5b) and -0.45 V (Fig. S12b). On Pd/VC-40, formate partial current density at -0.25 V almost doubles in comparison to -0.35 V (Fig. 5d), but this value is much lower than those obtained with Pd/SWCNT-40. Between the two carbon supports investigated, SWCNTs appear as a better support choice for obtaining larger amounts of formate, as most of the input energy goes into hydrogen evolution on the Pd/VC materials. On all occasions, the highest $\ensuremath{\text{FE}_{\text{HCOO-}}}$ and formate partial current density is observed during the initial 2 h of CO₂R (Fig. 5 and S12) and, upon further CO₂ reduction, the formate productivity drops drastically (Figs. S11 and S13). This is especially true for the Pd/SWCNT-40 material which exhibits a relatively high formate partial current density

during the initial 2 h CO₂R, *ca.* -12 mA cm^{-2} , but also a very significant 60 % drop during further CO₂ reduction. A similar drop in formate formation over time has been previously observed on a supported Pd₇₀Pt₃₀/C electrocatalyst [1] and on Pd [2]. At the same time, CO selectivity slightly improves over CO₂R duration (compare for example 0–2 h and 2–4 h FEs on Pd/SWCNT-0 in Fig. 5a and S11a).

Pd atoms bind strongly to CO, which results in a progressive deactivation of the catalytical properties of Pd nanostructures as their surfaces become poisoned. This is usually observed as a decrease in current density [34]. On all other materials except Pd/SWCNT-40, the recorded current densities decrease quickly during the initial 30–60 min of the CO₂ reduction reaction, indicating the deactivation of the catalyst surface (Fig. S15). However, for the Pd/SWCNT-40 electrocatalyst the current increases initially before also slowly decreasing over time. The initial increase could be caused by the gradual wetting of the hydrophilic electrode, thus, slowly increasing the accessible surface area during the first minutes. As was demonstrated by measuring the contact angle between the electrode and a drop of the electrolyte, Pd/SWCNT-40 is the most hydrophilic among the investigated electrodes. After becoming completely wetted and utilizing the maximum possible surface, the deactivation of the electrocatalyst would become visible as a slow current density decrease.

3.3. The effects of carbon and ozone treatment on CO_2 -to-syngas electroreduction

At highly negative potentials, Pd becomes a CO-selective electrocatalyst as can be seen from the FEs at applied potentials of -0.85 V in Fig. 6 and Fig. S16 and at -0.95 V in Figs. S17-18. All the studied catalysts also produce trace amounts of formate at these potentials. Whereas the ozone treatment seems to improve formate formation on the studied materials, the CO-selectivity has an opposite trend. At -0.85V, the FE_{CO} decreases as the ozonation duration is increased for both SWCNTs- and VC-supported materials (Fig. 6). At -0.95 V, FE_{CO} is comparable on Pd/SWCNTs, while a decreasing trend with increasing ozonation duration is still observed on the Pd/VC electrocatalysts (Fig. S17). Since the total current densities increase along with the ozonation duration, no major variations appear between the CO partial current densities measured on the different catalysts. Since carbon inevitably produces H₂, these catalysts could be ideal for syngas production. Especially Pd supported on the pristine carbon materials has desirable CO/H₂ ratios varying between 0.5 and 1.0 (Fig. 7). The obtained CO/H₂ ratios are in line with previous reports on Pd-based catalysts [33].

As described earlier, the FE_{CO} slightly increases with CO_2R duration. This can be also visualized when comparing the CO/H_2 syngas ratios in Fig. 7, where an increase in the ratio is observed for all studied electrocatalysts on both applied potentials when CO_2R is carried on beyond the initial 2 h. An increase in CO selectivity over time has been reported for a PdIn alloy with an In_2O_3 surface layer [45]. The variation of the current density over time on Pd/SWCNTs (Fig. S19 a and c) shows similar behavior as observed when applying the more positive potentials (Fig. S15 a and c). For the Pd/VC series, a drop during the initial minutes is followed by either a quite steady current (-0.85 V, Fig. S19b) or a slowly increasing current (-0.95 V, Fig. S19d). This increase can originate from several possible sources, including changes in the materials themselves. From our results, the VC-supported catalysts appear more relevant for application in syngas production.

3.4. Discussion of possible origins for the selectivity changes on the SWCNT support

The purpose of this section is to discuss the possible origins of the observed changes based on the obtained results tough a definitive answer about the reaction mechanisms cannot be given. In general, it is believed that hydrophobicity is required for efficient CO_2R since the reactions take place at the gas-solid-liquid triple-phase interphases. Based on our flow cell results, hydrophilicity of the substrate improves formate selectivity while hydrophobicity appears to improve CO selectivity especially with the SWCNT support. Pd nanoparticles on the studied materials are similar in morphology and crystal phase, and no electronic effect are observed in the XPS spectra (Fig. S9). The only observed differences between the SWCNT support.

It is known that four reactions can take place on Pd in the investigated potential range: the electrochemical reduction of CO_2 to CO and formate, the reduction of water to hydrogen, as well as the electrochemical hydrogenation of CO_2 [38,46]. Additionally, Pd can directly reduce HCO_3^- ions to formate [11] rather than using CO_2 directly as a feedstock. The possible routes are demonstrated in the supporting



Fig. 6. FEs (a and c) and partial current densities (b and d) at an applied potential of -0.85 V in 0.5 M KHCO₃(aq) over the initial 2 h of CO₂R on 20 wt% Pd supported on (a–b) SWCNTs and (c–d) VC treated with O₃ for varying durations.



Fig. 7. CO/H_2 syngas ratios over 4 h of CO_2R on 20 wt% Pd supported on (a–b) SWCNTs and (c–d) VC treated with O_3 for varying durations at applied potentials of -0.85 V (a and c) and -0.95 V (b and d) in 0.5 M KHCO₃(aq).

information (Scheme S1).

Additional flow cell experiments were performed without the presence of CO₂ to help elucidating possible origins for the observed changes. A reductive potential of -0.23 V (vs. RHE) was applied in N₂-saturated 0.5 M KHCO₃(aq) (pH = 9.7). The electrolysis results in generation of trace amounts of formate (Fig. S20a), which shows that formate route possibly does not require a gaseous reactant but a reactant in aqueous phase. The current over time is clearly more stable than in the presence of CO₂ (Fig. S20b) indicating that the route leading to COpoisoning is possibly eliminated. CO poisoning of Pd is also such a well-known and many times proven phenomena [1,2,8,17] that it is safe to assume that it takes place also on the studied catalysts resulting in the observed decrease of formate selectivity. Furthermore, applying a reductive potential of -0.83 V without the presence of CO₂ resulted in the production of mere H₂ (Fig. S21).

So, CO cannot be produced without the presence of CO₂ gas as a reactant. In general, the material showing the lowest formate selectivity shows the highest CO selectivity, already in the low overpotentials (Fig. 5a and S12). These are also the more hydrophobic materials in our study which better facilitate transport of a gaseous reactant. As highlighted above, the size and shape of the nanostructures are very similar, so it would be difficult to argue that Pd would have different active phases, speculated previously to be one possible origin in the selectivity change [3]. β -PdH is the majority phase at these potentials and it is suggested to weaken the binding energies of the intermediates to facilitate efficient syngas production [33]. It has been shown through in situ ATR-SEIRA method that differences in the CO coverage facilitated the changes in selectivity [6]; higher coverage results in improved CO formation and poorer formate selectivity. Unfortunately, we lack the method to conclusively prove this on our catalysts. To understand the selectivity, additional RDE experiments were performed according to Ref. [34], and the results are presented in Fig. S22. On Pd/SWCNT-40, the H desorption peak steadily decreases and finally disappears while the CO desorption peak around 0.85 V (vs. RHE) increases with increasing CO2 reduction time at -0.35 V. On Pd/SWCNT-0, the H desorption peak disappears already after 5 min of CO₂ reduction while two CO desorption peaks appear at around 0.45 V and 0.85 V. This indicates that CO-desorption takes place more readily (lower potential required) on Pd/SWCNT-0 than on Pd/SWCNT-40.

It is challenging to clearly establish whether the electrochemical reduction of CO_2 , the reduction of HCO_3^- , the electrochemical hydrogenation of CO_2 , or a combination of these is resulting in formate formation. All the intermedia in these reactions are similar (Scheme S1). The electrochemical hydrogenation of CO_2 and direct reduction of HCO_3^- require aqueous reactants and facilitation of aqueous reactant transport, both improved in hydrophilic electrodes. Based on the test without CO_2 gas, HCO_3^- could be a reactant and in the presence of CO_2 gas its concentration would be higher due to the bicarbonate balance (Scheme S2). On the other hand, we also know based on our previous studies with ozone treated supports and hydrogen evolution reaction

(HER) catalysts that wetting is beneficial for HER [37]. On Pd, it has been shown that high coverage of Hads promotes formate formation while the deactivation by CO poisoning slowly decreases the amount of Hads on Pd and thus decreases the formation of formate [34]. Such reaction route is corroborated by the performed additional RDE experiments (Fig. S22b). The RDE test also indicates that more H_{ads} is retained on the ozone treated material in comparison to non-treated material as hydrogen desorption peak is still present after 20 min of CO2R on Pd/SWCNT-40 while it disappears after 5 min of CO₂R on Pd/SWCNT-0. Improved electrochemical hydrogenation of CO₂ on the hydrophilic support could be a reason for improved formate selectivity. Again, the presence of different Pd hydride phases (α and β) has been proposed as one possible explanation for the changes in selectivity [38]. Under CO₂ reduction conditions, Pd is mainly in the β -PdH form [47] with some α -PdH still present but at similar concentrations between the different catalysts. Since the size and shape of the nanostructures on the studied catalysts are quite similar, they are all expected to transform into the same active PdH phase quite quickly after applying negative potentials [2]. Based on these results, the hydrophilicity of the support affects the selectivity.

4. Conclusions

We investigated the effects of the carbon support and its ozonation on the activity and selectivity of CO2 electroreduction on Pd nanostructures. By simply changing the supporting carbon or increasing its hydrophilicity through the addition of oxygen atoms into the structure, we revealed that the supported Pd electrocatalysts can be tuned into formate selective or syngas selective electrocatalysts. Furthermore, our results show that increasing the duration of the ozonation treatment, and thus the hydrophilicity of the support, increases the catalysts' selectivity towards formate while decreasing the selectivity towards CO. The activity of the investigated catalysts also exhibits a clear dependency on the ozonation treatment, indicating that oxygen surface functions are beneficial for the activity. We concluded that this was most likely due to enhanced wetting and thus improved mass transport in the ozone-treated supports. Unfortunately, the ozonation does not seem to bring any significant improvement concerning the poisoning of the catalytically active sites. Further improvements in the stability of the electrocatalysts could be brought about by investigating the addition of other metals that affect the binding of the poisonous intermediate.

CRediT authorship contribution statement

Milla Suominen: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Junjie Shi: Writing – review & editing, Investigation, Formal analysis. Jani Sainio: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. Amine Hammouali: Writing – review & editing, Investigation, Formal analysis. Lilian Moumaneix: Writing – review & editing, Investigation. **Anna Kobets:** Writing – review & editing, Investigation. **Tanja Kallio:** Writing – review & editing, Resources, Funding acquisition, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Mr. Viljami Juntunen and Mr. Robin Grund are gratefully acknowledged for help in laboratory. Funding from Jane and Aatos Erkko foundation (the USVA project) and Research Council of Finland (project no: 352955) are gratefully acknowledged. This work made use of Aalto University RawMatters, Bioeconomy and OtaNano Nanomicroscopy Center facilities.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtener.2024.101727.

Data availability

Data will be made available on request.

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