# Introducing sulphur surface groups in microporous carbons: A mechanistic study on carbide derived carbons

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## ARTICLE INFO

## ABSTRACT

The mechanisms of introducing sulphur surface groups in porous carbons was deduced from the model carbon material carbide derived carbon (CDC) based on titanium carbide. The electrophilic substitution reaction at the aromatic ring system was identified as the predominant mechanism, even in highly amorphous carbons. The finding was deduced from TG–MS and XPS analysis. Upon varying the aromaticity and the amount of oxygen surface groups of the porous carbons, no change in mechanism was observed. This neglects an effect of spatial hindrance of the electrophilic substitution reaction within micropores. The introduced sulphur groups were found to be highly acidic sulphonic acid groups, which enable the functionalized carbons to be used as solid acid catalysts. The performance evaluation of the functionalized carbons catalyst in the esterification reaction of levulinic acid with ethanol supported the mechanistic findings. The activity correlated with the amount of sulphuric acid groups. The maximum amount of $0.86$ mmol m$^{-2}$ and, thus, the highest activity was determined for the most graphitic porous carbon material.

## 1. Introduction

The interest of the scientific community in carbon materials and their manifold application in catalysis is increasingly high [1]. As major reasons can be seen, that carbon can either serve as a catalyst support or as a catalyst, itself [2–4]. Secondly, the electrical conductivity and chemical inertness against corrosive media suites the challenges for electrochemical applications. In fact, carbons are in the focus of sophisticated research as an electrode material within supercapacitors [5], solar cells [6] and low temperature fuel cells [5,7]. Finally, carbon as catalyst support shows the advantage of high hydrothermal stability, high surface area to disperse metals, a variable surface chemistry and good recycling possibilities of noble metals. This advantages are leveraged especially in several biomass conversions, the forefront of green chemistry. Recently reported examples are aqueous phase reforming of xylitol [8], biomass deoxygenation [9], hydrolysis of cellobiose [10] and selective oxidation of glucose [11], respectively. Other green chemistry applications are reported for, both, oxidative processes, like waste water cleaning, [12] and reductive processes, like the hydrodechlorination of 4-chlorophenol [13].

The production of biodiesel is another popular example for biomass conversion. Carbon based catalysts are reported to be a highly efficient catalyst for the esterification and transesterification within the production process [14–16]. This was achieved by the variable surface chemistry of carbon which enables carbons to be used as solid acid catalysts. Solid acids are considered as economic and therefore green alternative to homogeneous acid catalysis [17], which is classically used to catalyze esterification reactions. In order to increase the acidity, the surface chemistry of a carbon, which is crucial for almost any application [18,19] or modification process [20,21], could be addressed by numerous techniques [22]. A wet chemical treatment with oxidizing acids, like nitric acid and sulphuric acid, is often applied due to the high degree of functionalization achieved. While nitric acid can be applied to introduces foremost carboxylic and other oxygen groups to the surface, besides some nitrogen hetero doping [21], sulphuric acid additionally can incorporate a pronounced amount of sulphuric groups. Because the Brønsted acidic strength of oxidized sulphur groups is significantly higher than of carboxylic groups, the functionalization with sulfuric acid is generally applied for the preparation of carbonaceous solid acid catalysts. Acidic sulphur surface groups, which are reported in literature, are either sulphonic acid or organo sulphates [23].

Stability is an issue for this catalytic application as well. Graphene provides great stability and was studied excessively, already [23]. Many studies report on the possibilities and mechanisms of introducing sulphur groups to graphene oxide (GO) and reduced graphene oxide (rGO). A functionalization with concentrated sulphuric acid or oleum is the standard procedure. The highly reactive $SO_3$ is reported to be the

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active species in both cases. The reported mechanism depends on the dominant functional group. In rGO the aromaticity of graphene is dominant and in GO the hydroxyl groups are the participating functional group. The ideal mechanism on these planar materials is reported to be either an electrophilic substitution to the aromatic ring system ($S_E$) or a nucleophilic addition ($A_N$) of the hydroxyl groups, respectively. Although the mechanism of sulfonation was proposed back in the 1960's by Cerfontain [24], modern computational simulations suggest that spatial hindrance in micro pores of porous carbon materials could inhibit the formation of stable transition states in the $S_E$ mechanism, especially for the more stable bimolecular process. Such spatial hindrance is not present in planar graphene sheets. A destabilization of the transition state would favor rather a sulfatation than a sulfonation, introducing organo-sulfphates respectively. Thus for classical activated carbons, which are technically due to their low costs and high availability the most interesting high surface area carbonaceous material, the mechanism is unclear. As they range from being solely amorphous to showing local graphitic domains, which is of interest for the stability [25], understanding which sulfonation mechanism takes place for both kind of activated carbons is needed.

In this study carbide derived carbons (CDC) is used as well defined model material for amorphous and graphitized carbons. Based on the reactive extraction of titanium carbide (TiC) and through varying the synthesis temperature, porous carbon results with different degree of aromaticity [3,26]. This allows to shade light on possible mechanistic changes in sulfonation within micropores, which is not only relevant for the application of carbon as solid acids but for other applications as well.

## 2. Experimental

### 2.1. Synthesis of carbide derived carbon

The production of carbide derived carbons (CDC) was based on titanium carbide (TiC) particles. The TiC (2 μm, 99.95%) was purchased from Alfa Aesar. The carbide particles were placed in a hot wall tube reactor and reacted with chlorine at temperatures of 800 °C, 1000 °C, 1200 °C and 1300 °C. The resulting CDCs are highly pure carbons. The residual titanium content is below detection limit of thermogravimetric and XRD analysis. Details on the synthesis are provided elsewhere [20].

### 2.2. Surface functionalization

The surface of CDC was functionalized by wet chemical acid treatment with sulfuric acid (98 %), oleum (20%) or oleum (65%). Oleum (x%) is the name for a solution of x% sulphur trioxide ($SO_3$) in concentrated sulphuric acid. Chemicals were purchased from Sigma Aldrich. For each treatment, 1 g of carbon was put in a 50 ml two neck glass flask and heated to reaction temperature for 10 min under argon flushing. After this short drying step, 20 ml of acid was added. The mixture was stirred at 400 rpm for 2 h under a reflux condenser. The reaction temperature was 180 °C for sulfuric acid (98%) and oleum (20%), and 90 °C for oleum (65%). Temperature was lower for oleum (65%) as it is the boiling temperature at atmospheric pressure. Afterwards, the reaction mixture was cooled to room temperature. In case of sulfuric acid, it was diluted in the 10-fold volume of water, for oleum the mixture was cooled to 0 °C in an ice water bath and diluted in the 20-fold volume of ice water. Subsequently, the functionalized carbon particles were separated by filtration using a 0.2 μm nylon filter. The residue was washed three times with 50 ml of distilled water, dried overnight in at 50 °C and washed again with water using a soxhlet extractor for 24 h.

### 2.3. Material characterization

The thermogravimetric analysis (TGA) was performed in air atmo-

sphere, for temperature-programmed oxidation (TPO) of the carbon bulk material, and in helium atmosphere, for temperature-programmed desorption (TPD) of surface functional groups. The later was combined with an online quadrupole mass spectrometer (UGA, Stanford Research Systems) for off-gas analysis (TPD-MS). Both, TPO and TPD-MS was carried out in a thermogravimetric apparatus (TGA, STA 409, Netzsch) using alumina crucibles. For TPO, the samples were dried prior to analysis in a furnace at 50 °C. The analysis was conducted for a sample mass of 20 mg with a heating rate of 5 °C min$^{-1}$–900 °C at a constant mass flow rate of 80 cm$^3$ min$^{-1}$. For TPD-MS the samples were dried within the TGA itself at 100 °C for 1 h, prior to analysis. Subsequently, the samples were heated to 900 °C at 5 °C min$^{-1}$ while recording the evolution profiles of $H_2O$ ($m/z$ = 18), CO (28), $CO_2$ (44) and $SO_2$ (64). The quantitative analysis of the data in order to deduce the composition of surface functional groups on the carbon surface is described elsewhere [21]. Additionally, the data was corrected for carbon burn-off at temperatures higher than 500 °C.

The chemical analysis of the binding state of surface groups on the samples was conducted by X-ray photoelectron spectroscopy (XPS, SSX 100, Surface Science Laboratories Inc.). Monochromatic $K_\alpha$ radiation of aluminum was used at an energy of 9 kV and 10 mA. Survey spectra for elemental concentration were recorded at a pass energy of 150 eV with a resolution of 0.16 eV and a step size of 0.5 eV. High resolution binding spectra were recorded at a pass energy of 50 eV with a resolution of 0.054 eV and a step size of 0.1 eV.

Textural properties of the carbon prior and after functionalization was determined by $N_2$-physisorption at liquid nitrogen temperature (Nova 3000, Quantachrome). Prior functionalization, the samples were degassed before the analysis at 250 °C, while functionalized samples were degassed at only 140 °C for the same time of 4 h. Lower degassing temperature was applied in order to avoid alteration of the samples upon analysis by desorption of low stability surface groups, e.g. carboxylic acid.

### 2.4. Solid acid catalysis

The catalytic activity of the sulfonated carbons was assessed in the esterification of levulinic acid with ethanol to ethyl levulinate. The reaction was turned out in a 25 ml flask equipped with a reflux condenser. The reaction temperature was 60 °C and the reaction kinetic was analyzed by Gas Chromatography (GC, Varian 3900, FID detector, capillary column: Stabilwax-DA from Restek). For a typical reaction, 10.45 ml (0.179 mol) of ethanol was added to 4 g (0.0345 mol) of levulinic acid. After taking an initial sample for GC analysis, the reaction was started by adding 80 mg of the solid acid catalyst and placing the reaction mixture in a tempered oil bath. The amount of catalyst equals 2 wt% of the reactant levulinic acid, respectively. Samples of each 0.2 ml were taken after 20 min, 40 min, 1 h, 3 h and 5 h. The solid acid catalyst was instantly separated from the reaction mixture by using a syringe filter (0.2 μm, PTFE) and the permeate was diluted in a standard solution for GC analysis (0.1 M 2-pentanone in 1,4-dioxane). Each sample was measured by three independent injections and the data represents the arithmetical average.

## 3. Results and discussion

The mechanisms which are reported in literature for the insertion of sulphur groups to a carbon surface are shown in Fig. 1. Accordingly, sulphur is introduced by (a) either an electrophilic aromatic substitution or (b) a nucleophilic addition. In both cases, the active species is sulphur trioxide ($SO_3$). The substitution reaction takes place at the functional benzene group of carbon and yields sulfonic acid groups, whereas the addition reaction takes place at the functional hydroxyl group and yields organo sulphates. Both types of functional groups are present in the porous CDC materials at different shares.

The share of the functional benzene group could be approximated