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Preparation of carbide-derived carbon supported platinum catalysts

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ABSTRACT

Well defined carbon supported catalysts are of interest to deduce structure activity relationships and for catalyst optimization. Carbide-derived carbons (CDC) are high purity porous carbons with tunable pore structure. The deposition of platinum on silicon and titanium carbide based CDC was studied, using a three step process of acid treatment, ion-adsorption of platinum precursor and gas phase reduction. The influence of the steps on the carbon support properties and possibility to control the platinum loading and resulting cluster size was determined. Most crucial is the acid treatment step, where oxygen groups are introduced. At a too high degree of functionalization (non-carbon content above 30 wt%), which can result for nitric acid treatment, the pore structure is heavily attacked. For sulfuric acid treatments non-carbon contents below 15 wt% and only minor changes in the pore structure were observed. The ion-adsorption technique could be successfully transferred to the CDC supports. For medium to high degrees of functionalization (non-carbon contents above 20 wt%) the full deposition of 2.5 wt% of platinum was achieved. By the choice of platinum precursor, the pH of impregnation and the temperature of reduction the platinum cluster size could be varied from 2.5 to 5.3 nm. Thus, important knowledge how to prepare tuned Pt/C catalysts based on CDC and the ion-adsorption technique could be deduced.

1. Introduction

Porous carbon materials combine in an unique manner interesting properties like stability at hydrothermal, acidic and alkaline environment, low interactions with catalytically active species, high specific surface area as well as an easily modifiable surface, which makes them attractive as catalyst support [1–3]. An early application of carbons as catalysts support was the hydrotreating process, where carbon materials recently again attract attention [4,5]. Further large scale applications of carbon supported catalysts are e.g. the caprolactam production starting from toluene, where the hydrogenation of benzoic acid is carried out with Pd/C [6], hydrogenation of nitrobenzene for the production of aniline with various metals supported on carbon [7–9] or hydrogenation of dinitrotoluene to toluenediamine with platinum on carbon black for the polyurethane production [10]. Pt/C is employed in the nitrate and nitrite reduction for waste water treatment [11,12] and discussed for the application in hydrodechlorination [13]. Nevertheless, the most important fields of application are (i) fine chemical production [2,14] i.e. in the selective hydrogenation of α,β-unsaturated aldehydes [15,16], hydrogenation of sitosterol [17,18] or synthesis of sorbitol [19] and (ii) electrocatalysis [20,21].

Hereby two most common carbon materials are activated carbon and carbon black [2,10], as they are highly available and cheap. Yet especially for activated carbon the production leads to fluctiating material properties and limited reproducibility. As a result, performance of catalysts supported on activated carbon can vary strongly. This hinders straightforward determination of structure-activity relationships necessary to further accelerate catalyst optimization [22–24]. Furthermore a detailed characterization of every catalyst batch is necessary, making research very time and investment consuming. Hence, there is need for a model carbon material with highly reproducible and tunable material properties.

Carbide-derived carbon (CDC), where porous carbons are produced by the reactive extraction of carbides, meets all the previously described requirements. Specific surface areas of the materials are approximately between 1000 and 2000 $m^2 g^{-1}$ [25]. Typical extraction temperatures range between 400 and 1200 °C and can in combination with the choice of carbide precursor be used to tune the resulting pore structure from molecular sieve

Abbreviations: CDC, carbide-derived carbon; DTG, derivative thermogravimetry; FWHM, full width at half maximum; MPS, mean pore size; PZC, point of zero charge; SiC-CDC, silicon carbide-derived carbon; SPV, specific pore volume; SSA, specific surface area; TiC-CDC, titanium carbide-derived carbon; TPD, temperature programmed desorption.

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like characteristics towards mesoporous [25–28]. Material properties can be reproduced with high accuracy from batch to batch and CDC are available in a variety of shapes ranging from monoliths to films, foams, ordered mesoporous structures and nano- to macroscopic powders [29–32]. Besides, the carbons show only very minor impurities regarding surface functionalization and ash content [33].

First reports demonstrate the applicability of CDC in catalysis, i.e. without noble metal after sulfonation in the esterification of stearic acid with ethanol [32] or with dispersed noble metals (e.g. Pt, Pd, Ru, CeO_2/Pt) in the shape selective hydrogenation of olefins, [34], hydrogenation of 4-carboxybenzaldehyde [35], aqueous phase reforming of biomass [36], partial oxidation of methane or tetralin [32,37–40] and oxygen reduction reaction [37,41].

While CDC materials are already used to derive structure-activity relationships e.g. in the aqueous phase reforming, where the very low acidity let to an extraordinary hydrogen selectivity [36], systematic studies on deposition of noble metals on CDC supports, control of resulting catalyst properties and influence of the deposition procedure on the tuned CDC properties are missing, which is aim of this work. CDC produced from silicon carbide at 1000 °C (SiC-CDC-1000) and titanium carbide at 800, 1000 and 1200 °C (TiC-CDC-800, TiC-CDC-1000, TiC-CDC-1200) were used for the study. The former represents the cheapest CDC with a narrow pore size distribution in the ultramicropore range. The latter shows an increasing mean pore size with increasing synthesis temperature. The study focuses on platinum as active metal, due to its prominent role in catalysis. The ion exchange of platinum salts was chosen as deposition method as it is reported to allow control of metal cluster sizes and loadings [42–44]. In this multistep preparation method first the carbon support is oxidized to introduce functional surface groups, subsequently ionic platinum species are adsorbed from aqueous salt solutions by coulomb interactions with the support surface and finally the precursor is reduced to obtain metallic platinum on the support. All three steps are subject of this study.

2. Material and methods

2.1. Materials

Silicon carbide was purchased from Alfa Aesar with a purity >99% and a mean particle size of 38 μm, titanium carbide was purchased from Goodfellow with a purity >99.8% and a mean particle size of 85 μm. As platinum precursors, hexachloroplatinic acid H_2PtCl_6 and tetrammine platinum nitrate $[Pt(NH_3)_4](NO_3)_2$ were purchased from ABCR with a purity of 99.9%.

2.2. Synthesis of CDC

The reactive extraction of metal carbides was carried out in a tubular alumina reactor (inner diameter 32 mm) using chlorine gas as extraction agent. All experiments were conducted with a chlorine concentration of 1.5 mol m^{-3} in helium at a superficial velocity of 0.03 m s^{-1}. Silicon carbide was chlorinated at 1000 °C, titanium carbide at 800, 1000 and 1200 °C. After a reaction time of approximately 5 h typically 5 g of carbide were completely converted to ca. 1.5 g of SiC-CDC or 1 g of TiC-CDC, respectively. After chlorination, all materials were treated with H_2 at reaction temperature for 30 min in order to remove residual chlorine from the produced CDC and terminate its surface with hydrogen. All carbide materials were completely converted to carbon, which was proven by the mass loss during the chlorination reaction as well as by X-ray diffraction (XRD).

2.3. Oxidative pre-treatment

As post treatment CDC materials were oxidized in a suspension with nitric acid (65 wt%) or sulphuric acid (50 wt%) for 2 h at 90 °C using 50 ml of acid per 1 g of solid. A coil distillate condenser prevented evaporation. After the respective functionalization time, the flask was quenched to ambient temperature and the CDC separated from the acid by filtration. Afterwards, the CDC filter cake was washed with distilled water until the filtrate reached pH 7. The functionalized CDC materials were dried at 80 °C overnight.

2.4. Ion-adsorption

Regardless of the type of CDC the ratio of impregnation solution to carbon was always adjusted to 50 ml solution per g_{CDC}. As precursor materials either H_2PtCl_6 or $[Pt(NH_3)_4](NO_3)_2$ were dissolved in water leading to an either anionic or cationic precursor, respectively. The platinum precursor concentration was adjusted to a catalyst loading of 2.5 wt% of elemental platinum for full deposition. For H_2PtCl_6, the pH of the solution was adjusted to values below the point of zero charge (PZC) of the acid treated CDC using HCl and NaOH. In case of $[Pt(NH_3)_4](NO_3)_2$ the pH was raised above the PZC of CDC using HNO_3 and NaOH. After addition of the functionalized CDC the pH of the suspension was controlled and readjusted if necessary. The suspensions were stirred at room temperature for 24 h and filtered subsequently. The impregnated CDC filter cake was then washed with 200 ml water of equal pH as the impregnation solution, adjusted also with HCl or HNO_3 and NaOH and dried subsequently in an oven at 80 °C overnight.

2.5. Reduction

For reduction of the adsorbed ionic platinum species, the powder resulting from the ion-adsorption was reduced with hydrogen (20 vol% in nitrogen) in a tubular quartz glass reactor (inner diameter 32 mm) with a flow of 10 L_{STP} h^{-1}. If not stated differently 300 °C were employed.

2.6. Nomenclature of samples

For clarity, in this work sample abbreviation always contains information on the type of CDC, its chlorination temperature, the acid used within the oxidation and if platinum was deposited. As an example TiC-CDC obtained after 1000 °C chlorination, treatment with HNO_3 and impregnation with platinum would be referred to as Pt/TiC-CDC-1000-HNO_3.

2.7. Materials characterization

The analysis of the pore volume and pore size distribution was carried out for the CDC after synthesis, acid functionalization and platinum deposition, using N_2-sorption measurements with a Quantachrome QuadrasorbSI at 77 K. Subsequent data evaluation was performed with the software QuadraWin version 5.02, using Quenched Solid Density Functional Theory (QSDFT) for slit pores. A mean pore size (MPS) was calculated assuming slit pores with the specific pore volume (SPV) and the specific surface area (SSA) calculated with QSDFT from N_2-sorption: MPS = 2·SPV/SSA

The PZC was determined with the concept of infinite mass titration [45] using the pH electrode Polyplast Temp DIN from Hamilton in different suspensions of CDC in water starting from 0.01 up to 10 wt%.

The metal loading was obtained with inductively coupled plasma optical emission analysis. Therefore, the catalysts were treated with a mixture of 8 ml HF, 2 ml HNO_3 and 2 ml HCl for 24 h to dissolve the metal from the carbon surface. The solutions were