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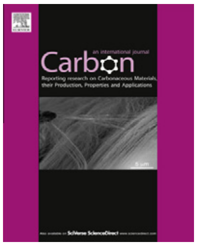

Transition metal loaded silicon carbide-derived carbons with enhanced catalytic properties

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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 m^2/g and 1.25 cm^3/g for Pt to 2480 m^2/g and 2.0 cm^3/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.

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

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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 m^2/g) and pore volumes (~0.64 cm^3/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 supercap applications. 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 value) [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 ($S_G < 16$ m^2/g), the corresponding CDC materials exhibit high surface areas between 1500 and 2500 m^2/g and pore volumes up to 2 cm^3/g (Table 1).

Especially CDC-Ru exhibits a very high specific surface area (up to 2480 m^2/g), and high micro- and total pore volume (up to 0.7 cm^3/g and 2.0 cm^3/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 ($S_g = 1420$ m^2/g; $V_{micro} = 0.56$ cm^3/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