



Control of porosity and composition of carbon based catalysts prepared by template assisted routes



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ABSTRACT

Carbon based catalysts for the oxidative dehydrogenation of ethylbenzene were prepared by a template assisted route. Using that synthesis procedure, the carbons could be modified systematically regarding their surface area and composition (namely the amount of nitrogen). Mesoporous silica and porous concrete, respectively, were used as the hard templates, whereas an aqueous solution of sucrose was the carbon source. Nitrogen was introduced by urea which partially replaced the sucrose in the solution. The materials were characterized by means of nitrogen adsorption at -196°C , X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and tested as catalysts in the oxidative dehydrogenation (ODH) of ethylbenzene. The catalytic activity was discussed with regard to the textural properties and the nitrogen content in the carbon catalysts.

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1. Introduction

Carbon materials have been widely investigated as catalysts for redox reactions such as the oxidative dehydrogenation (ODH) of hydrocarbons [1–5] or the electrochemical oxygen reduction [6–9]. The catalytic behavior of carbon based catalysts can be attributed to different features of these materials. A key role plays the graphitic species because they are important for the interplay of adsorption and activation of the reactants, especially oxygen. Here, the edge planes of the graphitic species are more active than the basal planes and oxygen can be chemisorbed more readily on the carbon atoms located there. However, before the chemisorption takes place the oxygen molecule must be activated and this can be done on the basal planes due to an electron interaction [10]. According to these concepts, the catalytic cycle of the ODH on carbon materials starts with the dehydrogenation of alkane molecule (e.g. ethylbenzene) on quinone-like centers under the formation of hydroxyl groups. In another step, gas phase oxygen is dissociated on the basal planes and then diffuses to the hydroxyl groups. The so activated oxygen can react with these groups with the formation of water and the reformation of the quinone-like groups. So, the redox pairs of

quinone/hydroquinone can be regarded as the catalytically active sites for the ODH [11–13].

The catalytic behavior of carbons can also be influenced by foreign atoms which form different functional groups distributed on the carbon surface. If nitrogen is incorporated into the aromatic rings of the carbon structure it can reduce the gap between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals and facilitate the electron transfer from the carbon material to the adsorbed oxygen species [14]. Recently, it has been shown that graphitic nitrogen enhances the catalytic activity of carbon nanotubes in the oxidative dehydrogenation of propane. This effect was attributed to a decrease in the overall activation energy and acceleration of oxygen activation [15].

It can be summarized that the catalytic behavior of carbon based catalysts in the ODH reaction is mainly affected by:

- the graphitic character of the material, because the edge planes of the graphitic species bear the redox pair quinone/hydroquinone which act as the active sites,
- the internal surface area because it correlates directly with the amount of active sites, and
- the nature and the amount of surface functional groups.

Consequently, for the systematic investigation of carbon based catalysts the interplay of these three features has to be considered. This has been the subject of a huge amount of publications so far.

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However, due to the broad diversity of carbon materials the comparability of the results reported in the literature turned out to be quite difficult. Thus, the development of a concept of a modular design of carbon catalysts, i.e. changing one feature while retaining the others, became a challenge in catalysis and material science. The template assisted synthesis route should be a useful tool for this purpose. This synthesis procedure includes several steps such as the pore filling of a porous template with a carbon precursor, its carbonization in oxygen-free atmosphere, and subsequent liberation of the carbon replica by dissolving the template in acids or bases [16–21]. Applying such route materials with different pore systems could be prepared. Using zeolites as the template highly microporous carbons with a BET surface area up to $3000\text{ m}^2\text{ g}^{-1}$ were obtained [17,19,20]. Ryoo et al. reported about the synthesis of mesoporous carbons with an ordered pore system which were prepared as the negative replica of ordered mesoporous silicas like MCM-48 [18]. A successful preparation of macroporous carbons using porous concrete as the hard template was reported by our group [16,22]. Very recently, that synthesis method has been extended by a simultaneous chemical activation of the carbon matrix which resulted in materials with the pore system ranged from the micropore up to the macropore region [23]. Due to the synthesis history of the material, a hierarchical arrangement of the pores has to be assumed: as the macropores should be mainly created by the template effect of the porous concrete, the micropores are rather the result of the activation process and should be located within the walls of the macropores.

In this contribution, we report about the template assisted synthesis of porous carbon catalysts for the ODH of ethylbenzene. Two series of catalysts were investigated: (i) carbons with different surface areas at similar composition and carbon structure, as well as (ii) carbons with varied content of nitrogen at similar surface area and carbon structure. The catalytic behavior of the materials was correlated with their properties determined by means of nitrogen adsorption at $-196\text{ }^\circ\text{C}$, X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Carbon synthesis

Two series of samples were prepared. In series 1 carbon materials with varied textural properties were prepared using porous concrete and silica gel, respectively, as the template. The carbon precursor was sucrose. In series 2 carbons were prepared from sucrose/urea mixtures to obtain carbons with different amounts of nitrogen. In this case, silica gel was used as the template.

The catalyst samples from silica gel template were prepared by the modified procedure described earlier in Ref. [24]. Briefly, mesoporous silica gel spheres (BET surface $330\text{ m}^2\text{ g}^{-1}$, total pore volume $1.0\text{ cm}^3\text{ g}^{-1}$) from Chemiewerk Bad Koestritz, Germany, were infiltrated with aqueous solutions of sucrose or sucrose/urea according to the pore volume of silica. The precursor concentration values are given in Table 1, respectively. After drying at room temperature for three days and carbonization at $600\text{ }^\circ\text{C}$ for 3 h (in flowing N_2) the carbon-silica composite samples were obtained. For some carbon-silica composites, a second and a third loading cycle including the same procedure (filling, drying, and carbonization) was applied to fill the remaining pore volume with carbon. Then, a thermal treatment at $900\text{ }^\circ\text{C}$ for 3 h (again in flowing N_2) finished the carbon synthesis by strengthening the carbon structure. The carbon replicas were deliberated by dissolution of the silica gel in HF (40%). Finally, all carbon samples were thoroughly rinsed with distilled water and dried at $100\text{ }^\circ\text{C}$ under vacuum.

Table 1
Parameters of the synthesis procedure for the studied samples.

Sample	Template	Precursor, loading procedure
P-S-453	Por. concrete	Sucrose $1 \times 68\%$
P-S-623	Por. concrete	Sucrose $1 \times 48\%$
P-S-646	Por. concrete	Sucrose $2 \times 48\%$
P-S-821	Por. concrete	Sucrose $1 \times 38\%$
P-S-1053	Por. concrete	Sucrose $1 \times 48\%$ + ZnCl_2 , $\text{Zn/C} = 0.3^a$
S-S-681	Silica gel	Sucrose $3 \times 50\%$
S-S-1119	Silica gel	Sucrose $1 \times 50\%$, H_2SO_4 catalyzed
S-S-1051	Silica gel	Sucrose $1 \times 50\%$
S-SU-2.0	Silica gel	Sucrose 49.2% + urea 1.1%
S-SU-3.2	Silica gel	Sucrose 48.0% + urea 2.6%
S-SU-5.0	Silica gel	Sucrose 42.6% + urea 10.0%

^a Weight ratio.

The catalyst samples from the porous concrete template were prepared using a commercial porous concrete (Ytong DIN 4166, Xella GmbH) which is delivered as panels. From the panels particles were obtained by crushing (jaw crusher, sieving, sieve fractions of 4.0–5.0 mm). The template samples were treated by hydrochloric acid (25%) which dissolves the calcium and aluminum containing concrete phases. The so treated material had a BET surface area of $130\text{ m}^2\text{ g}^{-1}$ and a total pore volume (estimated by ethanol infiltration) of $1.3\text{ cm}^3\text{ g}^{-1}$. The pore sizes of the concrete template were broadly distributed from mesopores to macropores [16,23]. The template particles and monoliths were then impregnated in a vacuum desiccator with aqueous solutions of sucrose or sucrose with ZnCl_2 as the activating agent. The precursor concentration values are given in Table 1. The applied infiltration procedure was very close to an incipient wetness infiltration because it has been finished when the outer surface of the template grains was slightly wetted by the precursor solution. The impregnated template samples were then calcined in a nitrogen stream in a two-step procedure. First, the samples were treated at $600\text{ }^\circ\text{C}$ to carbonize the sucrose. Some carbon-template-composites were then loaded again with the precursor solution. In the next step the samples were treated again in a nitrogen stream at $900\text{ }^\circ\text{C}$ to strengthen the carbon structure. After dissolving the template in hydrofluoric acid (40%) the samples were thoroughly rinsed in water to remove all rests of the activating agents.

The system of denotation is as follows: the first letter stands for the used template (P – porous concrete, S – silica gel), the second letter(s) for the precursor (S – sucrose, SU – sucrose/urea). The number is for the special characteristic of the sample, i.e. for series 1 the BET surface area and for series 2 the nitrogen amount in wt.%. In that sense, P-S-453 is the notation of a material obtained from porous concrete and sucrose with a BET surface area of $453\text{ m}^2\text{ g}^{-1}$. On the other hand, S-SU-3.2 is a material obtained from silica and sucrose/urea with a nitrogen amount of 3.2 wt.%.

2.2. Characterization

2.2.1. Texture – N_2 adsorption

Nitrogen adsorption and desorption isotherms were collected at $-196\text{ }^\circ\text{C}$ on a Micromeritics ASAP 2020 volumetric adsorption system. The total surface area was determined according the BET equation. The pore size distribution (PSD) was obtained from the adsorption branch of the nitrogen isotherm using the density functional theory assuming cylindrical pore geometry. The micropore volume was calculated according the Dubinin–Radushkevich model.

2.2.2. X-ray diffraction (XRD)

The crystalline structure of the materials was investigated by X-ray diffraction (XRD) with a Bruker D2 Phaser instrument. $\text{Cu K}\alpha$ radiation (wavelength $\lambda = 1.5418\text{ \AA}$) was used as an X-ray source.

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