

# Anchoring of a [Mn(*salen*)Cl] complex onto mesoporous carbon xerogels

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## Abstract

Carbon xerogels were synthesized by the conventional sol–gel approach using formaldehyde and resorcinol. The wet gel was dried by two different procedures followed by carbonization, leading to mesoporous carbon xerogels with considerably different pore size distributions. The materials were subsequently oxidized with air, in order to introduce functional groups on the surface, in particular phenols, anhydrides and carbonyls. The capacity of the carbon xerogels for direct immobilization of metal complexes was tested with a manganese(III) *salen* complex which possesses an extended ligand  $\pi$  system and two reactive hydroxyl groups on the aldehyde fragment. The manganese loadings of the various samples indicate that larger amounts of Mn(III) complex were immobilized in the oxidized carbon xerogels when compared with the parent unactivated materials, suggesting that complex immobilization took place preferably by covalent bond between the surface oxygen functional groups and the ligand reactive groups, rather than by  $\pi$ – $\pi$  interactions. The size and shape of the carbon xerogel pores were also shown to play an important role in the final loading of the manganese(III) *salen* complex.

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## 1. Introduction

Carbon materials such as activated carbons are well-known catalyst supports, especially for liquid phase reactions. Compared to the conventional inorganic supports, they offer, among others, the advantage of higher stability in acidic and basic media [1].

However, activated carbons derived from naturally occurring precursors cannot be easily produced in the form of monoliths or membranes, which are required for more advanced applications. This has led to a growing interest for polymer derived porous carbons, such as carbon aerogels and xerogels, which can be obtained by carbonization of organic aerogels prepared by sol–gel condensation of resorcinol and formaldehyde, as originally described by Pekala [2]. As shown in recent reports, both the porous texture [3–5] and the surface chemical structure of these materials [6] can be tailored to suit specific needs.

Carbon aerogels and xerogels possess excellent characteristics as catalyst supports, such as high surface area (400–1200 m<sup>2</sup>/g), high porosity (>50%), open pore network, controllable pore size, high density (0.6–0.8 g/cm<sup>3</sup>), they are electrically conductive and can be prepared in the desired form (monolith, thin film or powder). The preparation of metal-doped carbon aerogels, and their applications in catalysis were reviewed by Moreno-Castilla and Maldonado-Hódar [7], while the preparation and performances of carbon xerogel supported metal catalysts were the subject of various recent publications [8–13].

We have been exploiting the surface properties of activated carbons for the immobilization of transition metal complexes with *salen* type ligands using different immobilization strategies [14–18]. Similar methodologies were used by Román-Martínez et al. to anchor a Rh complex onto an activated carbon support [19]. The activated carbons with immobilized metal complexes with catalytic properties were found to be efficient and re-usable in various catalytic reactions [16–18]. However, in general, the slow diffusion of reactants through the micropores of activated carbon supports makes the heterogenized catalysts less active than the corresponding homogeneous cat-

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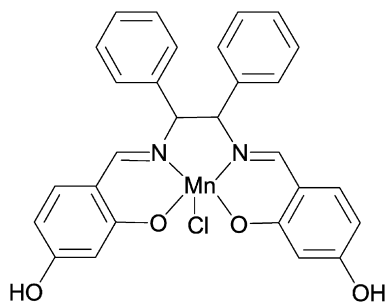


Fig. 1. Molecular structure of the manganese(III) *salen* complex.

alysts. This limitation can be overcome by using mesoporous carbon materials as supports for metal complexes, as diffusion of the reactant and product molecules are expected to be much easier through the wider pores.

In the present work, we report on the preparation and characterization of two different types of mesoporous carbon xerogels (CX) having different pore texture, to be tested for direct immobilization of a manganese(III) *salen* complex in which the ligand has an extended  $\pi$  system and two reactive hydroxyl groups on the aldehyde fragment (Fig. 1); by choosing this complex we endeavor to test two potential immobilization methodologies: (a) by  $\pi$ - $\pi$  interaction between the extended ligand and carbon  $\pi$  systems; and/or (b) by covalent bond between carbon xerogel surface oxygen functional groups and the ligand reactive groups.

## 2. Experimental

### 2.1. Synthesis of mesoporous carbon

Two types of mesoporous carbons (01CX and 02CX) were prepared by conventional sol-gel technique using formaldehyde and resorcinol following two different methodologies. Published procedures [3,6] were simplified and applied in this study. Synthesis of the wet gels and subsequent drying procedures were varied. The dried gels obtained in two different ways were pyrolyzed in the same fashion to obtain mesoporous carbon materials.

The xerogel leading to 01CX was prepared as follows: 29.73 g (270 mmol) resorcinol was dissolved in 57 cm<sup>3</sup> distilled water under magnetic stirring. After dissolution the pH was close to 3. The pH was increased to 5.8 by addition of 2 M NaOH solution. 40.6 cm<sup>3</sup> formaldehyde (500 mmol) solution (37 wt%; containing 10–15% MeOH) was added to the resorcinol solution with continuous stirring. The pH was adjusted to 6.0 by addition of 0.5 M NaOH solution. Stirring continued for 90 min, then it was stopped, the magnetic bar was removed, and the content was left for 3 days in an oil bath at 85 °C to perform the gelation. The hard gel was then ground to preferred size and dried in an air oven for a period of 7 days (1st day at 60 °C, 2nd day at 80 °C, 3rd day at 100 °C, 4th day at 120 °C, and 5th–7th days at 150 °C).

The xerogel leading to 02CX was synthesized by the following procedure: 33.04 g (300 mmol) resorcinol was dissolved

in 30 cm<sup>3</sup> distilled water. 49 cm<sup>3</sup> formaldehyde (604 mmol) solution (37 wt%; containing 10–15% MeOH) was added to the resorcinol solution with continuous stirring. The pH was measured at that stage (3.01). 0.159 g (1.5 mmol) Na<sub>2</sub>CO<sub>3</sub>, dissolved in 5 cm<sup>3</sup> distilled water, was then added. The pH was measured again (6.85). Stirring continued for 90 min, and then it was stopped. The gelling and curing step was performed in an oil bath for a period of three days (30, 50, and 90 °C, one day each). The hard gel was ground to preferred size. It was then washed twice with acetone containing 5% acetic acid; washing was continued several times for a period of 6 h with pure acetone. Thus an acetone filled gel was obtained, which was then further exchanged several times with cyclohexane to remove the acetone, for a period of 6 h. Cyclohexane was slowly removed, first by evaporation at ambient temperature, and then at 60 °C for 5 h to obtain the dried gel.

Mesoporous carbon samples were obtained by pyrolyzing the dried gels under nitrogen flow (100 cm<sup>3</sup> min<sup>-1</sup>) at 800 °C in a tubular furnace. The heating program included the following sequential steps in flowing nitrogen: (1) ramp at 2 °C min<sup>-1</sup> to 150 °C and hold for 60 min; (2) ramp at 2 °C min<sup>-1</sup> to 400 °C and hold for 60 min; (3) ramp at 2 °C min<sup>-1</sup> to 600 °C and hold for 60 min; (4) ramp at 2 °C min<sup>-1</sup> to 800 °C and hold for 360 min; (5) cool slowly to room temperature.

### 2.2. Gas phase activation

Activation of the carbon materials was performed under diluted oxygen flow (in nitrogen) to generate surface oxygen groups. Carbon samples were heated to selected temperatures at the heating rate of 10 °C min<sup>-1</sup> under 5% O<sub>2</sub> (in N<sub>2</sub>) and holding isothermally for different periods of time to achieve surface activated carbons of desired burn-off (BO). The BO was determined in each case by weighing the samples before and after activation. Henceforth the original unactivated carbon materials will be designated as 01CX-UA and 02CX-UA (UA stands for “unactivated”). Surface activated samples, 01CX-03 and 01CX-16 (03 and 16 are %BO values), were obtained from 01CX-UA by employing the activation course at 400 °C for 40 h and 440 °C for 40 h, respectively. Portions of the sample 02CX-UA were subjected to the activation course of 400 °C for 40 h and 440 °C for 30 h to obtain the surface activated samples 02CX-10 and 02CX-16, respectively (again, 10 and 16 are the %BO values).

### 2.3. Anchoring of the manganese(III) *salen* complex

The *salen* ligand and its manganese(III) complex were synthesized according to the procedures already described [18]. The Mn(III) *salen* complex was directly immobilized onto the supports by refluxing for 30 h 1 g of each carbon xerogel with 100 mg (185  $\mu$ mol) of Mn(III) *salen* complex in 150 cm<sup>3</sup> acetone. The resulting materials were Soxhlet extracted with acetone for 12 h, in order to remove any physically adsorbed complex, and finally the materials were dried at 120 °C.

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