

# PREPARATION OF SILICALITE MEMBRANES SUPPORTED ON GRAPHITE DISCS.

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## Introduction

Gas separation processes are often necessary in industry. Very different types of membranes have been designed for this purpose. Inorganic membranes have demonstrated good properties in the separation and catalysis of a wide number of processes. These membranes are specially useful for their stability at high temperature and aggressive environments[1].

Zeolites are microporous solids widely used as molecular sieves due to their 3D framework which forms channels[2]. The preparation of a thin layer of zeolite supported on an inorganic material gives us the unique properties of the zeolites as molecular sieves as well as catalysts and ion exchangers. In the 80's the preparation of zeolites supported in different inorganic materials has been reported, see as example refs. [3-4]. The applicability of these materials for gas separation has been also demonstrated for a wide number of systems[1].

Usually, the supports used are polymers or ceramics, which might present important disadvantages. Thus, polymeric supports have both low thermal and chemical stabilities and, though ceramics are more stable, they are expensive and brittle materials[1].

Carbon could be an interesting alternative to these materials due to its unique properties, such as the thermal stability in a non oxidizing environment, high stability in strong acids and bases, low expansion coefficient and the possibility to control its surface chemistry and porosity.

However, there are few studies devoted to the synthesis of zeolites on carbon materials, due, probably, to the difficulty of growing zeolites on hydrophobic surfaces. In this study, the synthesis of zeolite membranes supported on carbon will be analyzed in terms of the influence of the carbon surface chemistry on zeolite growth.

## Experimental

Macroporous graphite discs have been prepared from graphite powder and phenolic resin. These components have been intimately mixed and compacted by uniaxial pressure. The discs have been treated in air at 423K for 12h for resin curing and then in N<sub>2</sub> at 1073K for 12h.

To increase the hydrophilia of the carbon component, only one side of the carbon disc has been oxidized by different methods, as HNO<sub>3</sub> 70%, H<sub>2</sub>O<sub>2</sub>: HCl (1:1), both at room temperature for two days and air at 373K for 12 hours.

The graphite discs have been characterized by optical microscopy, SEM and Temperature Programmed Desorption (TPD).

The carbon discs have been immersed in a silicalite synthesis solution for three hours (ageing time). Different hydrothermal synthesis conditions (synthesis solution, temperature and time) have been tried to control the silicalite layer thickness.

## Results and Discussion

The direct hydrothermal synthesis of silicalite on the oxidized carbons produces a continuous layer of this material grown on the oxidized surface of the carbon disc. This zeolite-carbon composite has been characterized by XRD, SEM and DR-FTIR.

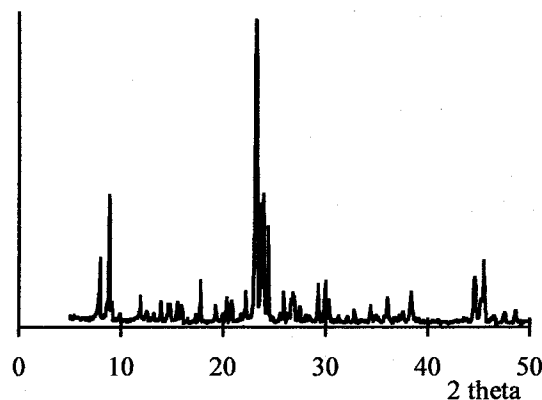


Fig. 1. XRD plot of the silicalite-carbon membrane.

The XRD pattern of the silicalite-carbon membrane obtained after 24h at 433K is shown in Figure 1. This plot corresponds to the crystalline structure of the silicalite (MFI type structure). XRD and FTIR confirm that silicalite has been selectively supported on the carbon surface.

The mechanical stability of the composite, that is the adherence between the silicalite and the carbon surface, has been confirmed by ultrasonic treatment for 15 minutes.

The morphology of the membranes has been observed by SEM. Figure 2 shows a cross section view of a polished silicalite/carbon membrane. A continuous layer of silicalite (see upper layer) is observed. The crystal size and layer thickness can be controlled modifying the synthesis conditions as usually in zeolite preparation.

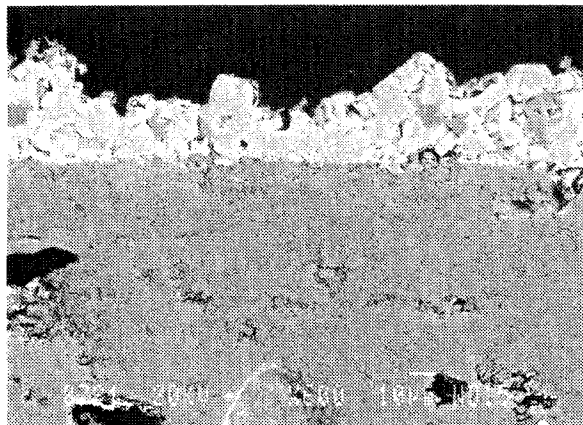


Fig. 2 SEM image of the cross section of the silicalite/carbon membrane.

Figure 3 shows the morphology of the upper surface of the material. Typical silicalite crystals are observed forming a continuous layer. Silicalite layers have been successfully grown only on the oxidized carbons. All the oxidizing methods tested, i.e.  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and air at 573K allowed us to obtain a hydrophilic carbon surface to grow silicalite on it. However, the original carbon discs, which have been treated in  $\text{N}_2$  at 1073K, and contain little surface oxygen groups, are not suitable to support silicalite.

In consequence, the presence of surface oxygen groups on the carbon discs is necessary to prepare a continuous layer of silicate. It seems that in the first steps of the zeolite formation the silicate chains react with carbon surface oxygen groups favouring the adherence of the silicalite crystal on the carbon surface.

To deepen into the influence of carbon surface oxygen groups on the silicalite-carbon interaction, oxidized carbon discs were treated in  $\text{N}_2$  at 773K to remove most of the acidic groups from the carbon surface. After that, the discs were immersed in the silicalite synthesis solution and subjected to the hydrothermal synthesis procedure. The characterization of the final product indicates the presence of a continuous silicalite layer supported on the carbon disc with good adherence. Thus, the stable

remaining oxygen groups are also efficient anchorage centers for nucleation and further growth of silicalite crystals.

## Conclusions

In conclusion, silicalite/carbon membranes have been successfully synthesized by the hydrothermal method. To achieve the proper growth of silicalite crystals it is necessary the existence of oxygen surface groups to increase the hydrophilia of the surface and produce anchorage centers. The obtained materials can be of interest as membranes for the separation of gases.

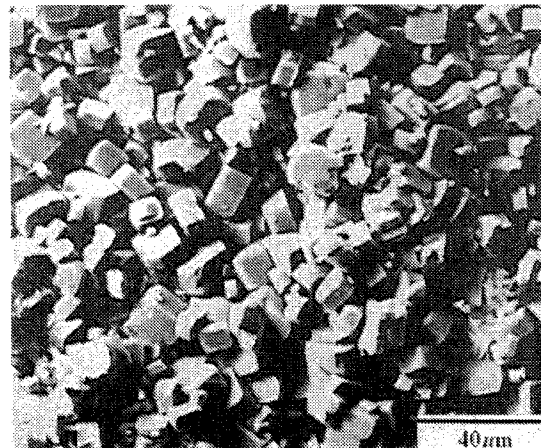


Fig. 3. SEM image of the upper surface of the silicalite/carbon membrane.

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