

# Avoiding Mass Transfer Limitations in Carbon Supported Catalysis by Using Carbon Xerogel as Supports

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## Abstract

Porous carbon materials with tailored pore texture can be prepared by evaporative drying and pyrolysis of resorcinol–formaldehyde aqueous gels. The pore size is easily controlled by the pH of the precursor solution. These materials, called “carbon xerogels”, can be used as catalyst supports, like activated carbons. Since the texture of these materials is adjustable, it is possible to avoid diffusional limitations that are often encountered when a microporous activated carbon is used as support by choosing a support with the appropriate pore size. The meso- or macropore size of carbon xerogels can be enlarged so as to simplify the reactant diffusion, which leads to better catalytic performances.

## INTRODUCTION

Porous carbon xerogels with tailored texture can be obtained by evaporative drying and pyrolysis of resorcinol–formaldehyde aqueous gels [1, 2]. The pore texture is controllable by varying the initial pH of the precursors solution in a narrow range: depending on the pH, micro-macroporous, micro-mesoporous, microporous or non-porous carbons are obtained. Solvent removal can be performed by the convective air drying process, which is commonly used in industry and very suitable to large-scale applications [3, 4]. The pore texture is not influenced by the drying conditions. Due to their pore texture flexibility and mechanical resistance, these materials are suitable for many applications, among which there are catalyst supports [5–8]. Moreover, the synthesis method is very simple and relatively cheap: large-scale production can be envisaged.

The ability to control at will the pore size in carbon xerogels is a great advantage compared to classical active charcoals, whose textural parameters are mainly fixed by the origin of the raw material to be pyrolyzed.

Moreover, these supports are mainly microporous, with low meso- or macropore volume. Even if the metal is well dispersed in micropores, mass transfer limitations decrease the apparent activity and modify the selectivity of the catalyst. On the contrary, the presence of large amounts of meso- or macropores should minimize diffusional limitations inside carbon supports synthesized by sol-gel process, and these supports could be designed according to the considered reaction. The aim of this work is to show that choosing a porous carbon xerogel with an adequate pore texture leads to the elimination of the diffusional limitations that are often encountered when activated carbons are used as catalyst supports.

## EXPERIMENTAL

Aqueous organic gels were synthesized by polycondensation of resorcinol with formaldehyde solubilized in water following a procedure described elsewhere [1]. The dilution ratio, *i.e.* the solvent/(resorcinol + formaldehyde) molar ratio, and the resorcinol/formaldehyde

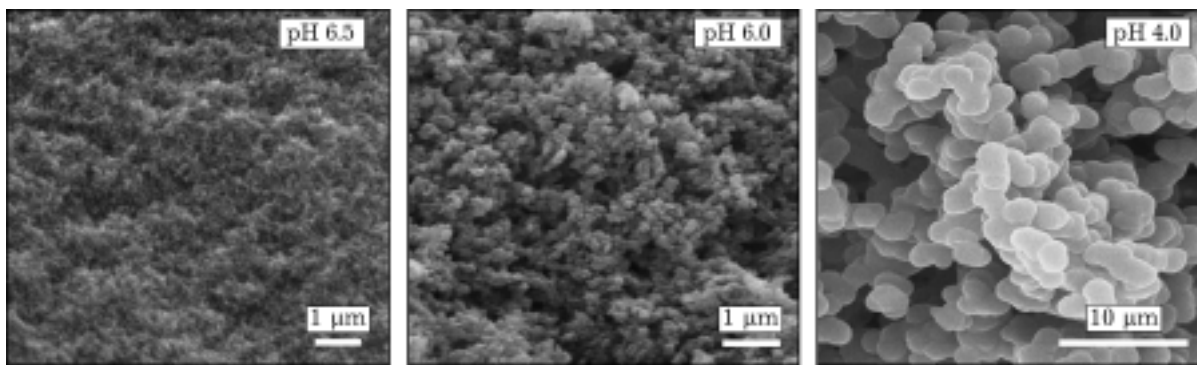


Fig. 1. Morphology of carbon xerogels after drying and pyrolysis of aqueous gels prepared in the presence of NaOH at various initial pH values. Synthesis temperature is 70 °C, dilution ratio is 5.7, pyrolysis at 800 °C under nitrogen flow.

molar ratio were fixed at 5.7 and 0.5, respectively. The initial pH of the precursors solution was adjusted at the chosen value with NaOH; the pH range for the gel series was fixed between 4.0 and 6.5. After gelation at 70 °C, the samples were dried and pyrolyzed at 800 °C under nitrogen flow for 3 h in order to obtain porous carbon xerogels.

Carbon xerogel pellets (diameter: 1000–1250 μm) were obtained by crushing and sieving the obtained carbon materials. Very well dispersed metal catalysts were prepared by impregnation of such pellets with aqueous solutions containing a salt of the desired metal. After impregnation and drying, the metal ions were reduced under H<sub>2</sub> in order to obtain the active phase. For example, Pt/C or Pd–Ag/C catalysts were obtained in previous studies [6–8].

## RESULTS AND DISCUSSION

Figure 1 shows the morphology of carbon xerogels obtained by evaporative drying and pyrolysis of resorcinol–formaldehyde aqueous gels. The materials are constituted of spherical-like interconnected nodules. The size of the nodules depends on the pH of the precursor solution: as the pH decreases, the nodule size increases. The nodule size range is very wide: from a few nanometers at pH ~ 7.0 to a few micrometers at pH ~ 4.0. Nitrogen adsorption measurements show that the carbon samples are micro-mesoporous or micro-macroporous: the meso- or macropores correspond to the voids between the nodules while the micropores correspond to the nodule inner porosity [1, 2]. The micropore volume is totally independent of

the pH of the precursor solution. On the contrary, the total pore volume and meso- or macropore size strongly depend on the synthesis conditions. Figure 2 shows the total pore volume and mean meso- or macropore size as a function of the solution pH. In parallel with the nodule size, the mean pore size increases from a few nanometers to a few micrometers when the pH decreases from 4.0 to 7.0. The total pore volume is maximal at pH < 5.0, and equals 2.2 cm<sup>3</sup>/g, which corresponds to the pore volume obtained without sample shrinkage [2]: the pore size in the wet gel is so large that the capillary forces due to curved liquid–vapour interfaces are negligible compared to the polymer mechanical resistance. At pH > 5.0, the pore size is smaller, and gas–liquid interfaces induce larger capillary forces that cause the sample to shrink; this is why the total pore volume decreases. However, despite shrinkage, the carbon materials obtained after drying and pyrolysis remain porous, and the size of the voids located between the carbon

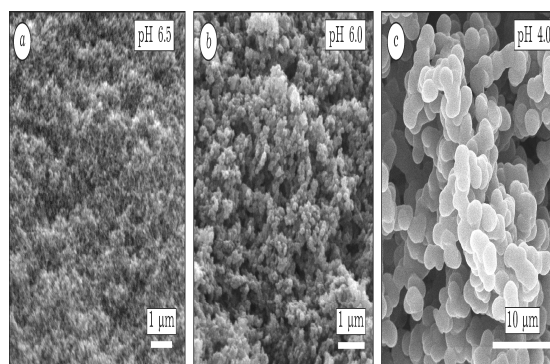


Fig. 2. Pore texture of carbon xerogels: total pore volume and mean pore size (micropores excluded) as a function of the pH of the precursor solution.

nodules is controllable *via* the pH of the resorcinol–formaldehyde aqueous solution.

Very well dispersed metal or alloy catalysts were obtained by simple impregnation with aqueous solutions of metal salts without oxidation pre-treatment [6–8]. Usually, activated charcoals are oxidized prior to impregnation in order to enhance the ion–carbon interactions and to increase the hydrophilic characteristics of the support when a polar solvent, like water for instance, is used [9]. However, despite the low amount of oxygenated surface groups present in carbon xerogels, these materials are extremely hydrophilic [8]. Indeed, carbon xerogels absorb 95 % of their total pore volume in a few minutes. Moreover, oxygenated groups tend to favour the metal sintering during reduction treatments when they resist to the reduction conditions [10]: the presence of oxygenated surface groups leads to the delocalisation of the *p*-electrons of the carbon, which are responsible for the anchoring of the reduced metal particles. Sintering is thus favoured when the support is strongly oxidized, which is not the case for carbon xerogels: the amount of oxygenated groups that resist to reduction at 350 °C (lactone, quinone, phenol, carbonyl, *etc.*) is about 10 times lower in carbon xerogels than in pre-oxidized active charcoals [8]. As a consequence, when deposited on carbon xerogels, the metal remains well dispersed.

During a catalysed reaction, the reactants must diffuse from the pellet external surface to the metal particles through the pellet porosity. This mechanism is often responsible for mass transfer diffusional limitations during the reaction: when the reaction rate is high compared to the reactant diffusion rate, and when the pathway between the external surface of the pellet and the metal particles is long, concentration gradients develop across the pellet section. As a consequence, the metal particles located in the centre of the pellet are less efficient than those located close to the pellet surface, and the global catalyst efficiency decreases. In other words, the global reaction rate measured at the reactor outlet (apparent reaction rate) is lower than the reaction rate at the surface of the metal particle (intrinsic reaction rate). This is frequently encountered when activated carbon pellets are used as

catalyst supports, due to the predominantly microporous pore texture of that kind of material. One possibility is to use powder catalysts instead of pellets: this reduces the mean distance between the reactants flow and the metal particles. However, this is not always possible, in particular in the case of fixed bed reactors, because of the large pressure drop.

Another way to avoid mass transfer limitations is to increase the pore size. When the pore diameter is lower than 100 nm, the diffusion phenomenon in the pores depends on both the ordinary gas diffusion and the Knudsen diffusion mechanism [11]: the mean free path of the diffusing species is lower than the pore dimension, which causes the molecules to hit the pore walls and to be randomly redirected. The smaller the pores, the more predominant the Knudsen diffusion. When the Knudsen diffusion mechanism occurs, the diffusivity in the pore (*D*) can be developed as a combination of both the molecular and the Knudsen diffusivities (Bosanquet formula [11]) as follows:

$$\frac{1}{D} = \frac{1}{D_m} + \frac{1}{D_K} = \frac{1}{D_m} + \frac{2}{97 \times 10^{-3} w (T/M)^{1/2}} \quad (1)$$

where  $D_m$  is the molecular diffusivity,  $D_K$  is the Knudsen diffusivity,  $w$  is the pore size,  $T$  is the temperature and  $M$  is the molecular mass of the diffusing species. Since the pore texture of carbon xerogels can be accurately tailored by changing the pH of the precursor solution, one can imagine decreasing the importance of the Knudsen mechanism contribution to the diffusion in the pores by enlarging the voids between the carbon nodules.

In order to study mass transfer inside a porous catalyst, the catalyst pellet is usually regarded as a pseudo-continuum, *i.e.* a pseudo-homogeneous medium in which the diffusion of a species is described by the same single diffusion coefficient, the diffusion mechanism being modelled by Fick's law. The fluid molecular diffusivity in the pseudo-homogeneous medium is thus replaced by the effective diffusivity ( $D_e$ ), which depends on the catalyst support morphology, and more particularly on the void fraction ( $\epsilon$ ), and on the tortuosity factor of the support ( $\tau$ ). The effective diffusivity is the diffusivity in the pores ( $D$ ) corrected by these two parameters:

$$D_e = \frac{\varepsilon}{\tau} D \quad (2)$$

Usually,  $\tau$  is considered equal to  $1/\varepsilon$  [11].

The concept of pseudo-homogeneous medium implies that  $D_e$  is the same everywhere in the pellet and that the considered length scale for mass transfer is the pellet size. However, the metal particles can be located either at the surface of the carbon nodules, *i.e.* in the mesopores or in the macropores, or in the microporosity developed within the carbon nodules. This configuration does not allow the use of the pseudo-homogeneous concept for the whole pellet. Since carbon xerogels are composed of spherical-like interconnected carbon nodules whose size can vary from a few nanometers to a few micrometers, one can consider a hierarchical texture composed of two distinct levels: a first one corresponding to the pellet itself, and a second one corresponding to the microporous carbon nodules (Fig. 3). Each level is characterized by its own density ( $\rho$ ), pore size ( $w$ ), void fraction ( $\varepsilon$ ), and length scale ( $L$ ). In the following discussion, a subscript “p” or “n” distinguishes the pellet level from the nodule level. Note that the considered “length scale” is the ratio between the volume and the external surface of the considered porous object. If both the pellet and the nodule are considered as spheres with a diameter equal to  $d_p$  and  $d_n$ , respectively, thus  $L_p = d_p/6$  and  $L_n = d_n/6$ .

Diffusional limitations are usually analysed through the use of the Weisz modulus ( $\Phi$ ),

which compares the observed reaction rate to the diffusion rate [11]. When  $\Phi \ll 1$ , the diffusion phenomenon is not significant and the observed reaction rate is equal to the intrinsic reaction rate. When  $\Phi \gg 1$ , diffusional limitations modify the apparent kinetics, and the observed reaction rate can be very different from the intrinsic reaction rate. Since carbon xerogels are composed of two distinct levels,  $\Phi$  must be calculated at both levels as follows:

$$\Phi_p = \frac{r \rho_p L_p^2}{D_{e,p} C_{sp}} \quad \text{and} \quad \Phi_n = \frac{r \rho_n L_n^2}{D_{e,n} C_{sn}} \quad (3)$$

where  $r$  is the observed reaction rate,  $C_{sp}$  is the reactant concentration at the external surface of the pellet and  $C_{sn}$  is the reactant concentration at the external surface of the nodule. In the case where diffusional limitations occur at the pellet level,  $C_{sn}$  can be evaluated from concentration profiles through the evaluation of the Thiele modulus [11].

The advantage of this method is that all the parameters are accessible to the experimenter, either by measurement or by calculation. The knowledge of the intrinsic reaction rate is not required. For example, Weisz moduli were calculated at both levels in the case of Pd–Ag alloy catalysts supported on carbon xerogels with various pore textures [6]: hydrodechlorination of 1,2-dichloroethane was used as a test reaction, and the tests were conducted on three catalysts with various meso- or macropore sizes (10, 30 and 70 nm), and

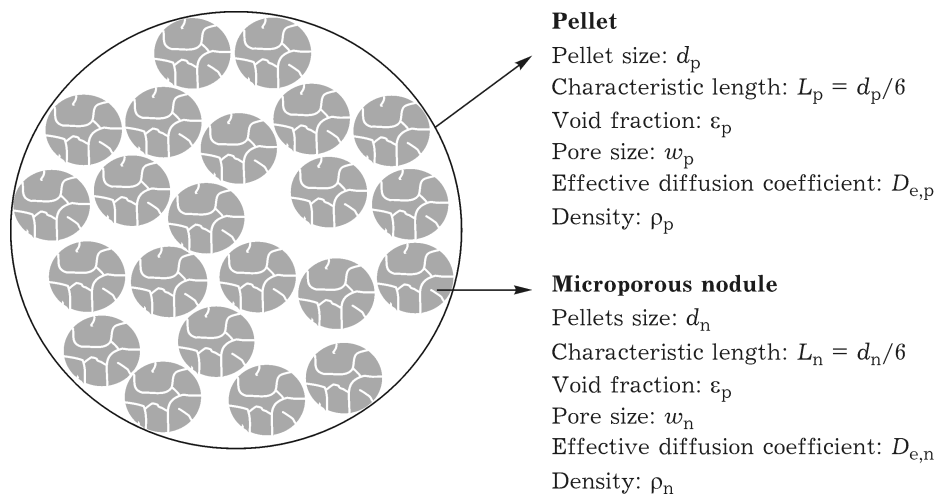


Fig. 3. Modelization of the catalyst pellet: two-level model.

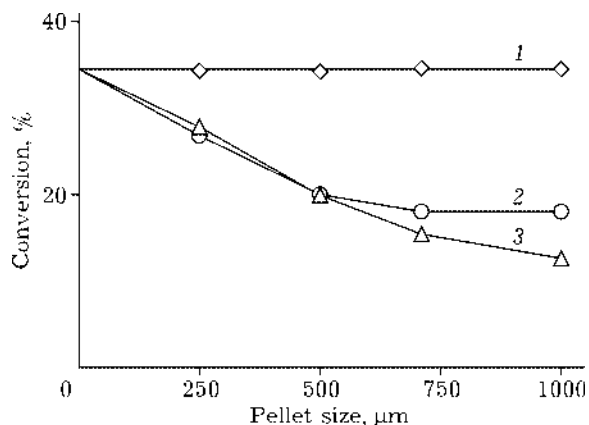


Fig. 4. Conversion of 1,2-dichloroethane as a function of the pellet size for 1.5 mass % Pd-3 mass % Ag catalysts at 350 °C. Supports: 1 - macroporous carbon xerogel (pore size is 70 nm), 2 - mesoporous carbon xerogel (pore size is 10 nm), 3 - activated carbon. Total flow rate: 40 Nl/h; gas ratio: He/H<sub>2</sub>/CH<sub>2</sub>Cl-CH<sub>2</sub>Cl = 37 : 2 : 1.

with pellets of increasing size. The results were compared to those obtained with similar bimetallic catalysts supported on activated carbon. Figure 4 shows that, when increasing the size of the pellets from 250 to 1000 μm, the activity of the catalysts supported on the microporous activated carbon and on the mesoporous xerogels decreases. In parallel, the Weisz moduli at the pellet level, calculated under the same conditions, get close to or larger than unity. This highlights the presence of diffusional limitations during the reaction at the pellet level, *i.e.* in the mesopores. On the contrary, the macroporous xerogel-type support led to the same conversion values, whatever the pellet size, which shows that diffusional limitations were eliminated in this case. Calculation shows that, in the case of the macroporous carbon xerogel (pore size is 70 nm), the conversion of 1,2-dichloroethane remains completely independent from the pellet size up to about 7 mm at 300 °C and 4 mm at 350 °C.

At the nodule level, the Weisz modulus was always much lower than 1: from 10<sup>-9</sup> to 10<sup>-3</sup>, depending on the reaction conditions and on the size of the carbon nodules. This shows that diffusional limitations, when detected *via* a loss of conversion with regard to a catalyst working in chemical regime, is due to slow diffusion in the largest pore class (mesopores or macropores). This apparent paradox can be explained by the

difference of path length to be covered by the reactants in meso- or macropores (several micrometers) and in micropores (several nanometers).

The use of carbon xerogels as catalyst supports can be extended to other catalyst/reaction systems, and the evaluation of the Weisz modulus following the above-described method can be used to determine whether mass transfer limitations occur or not.

## CONCLUSIONS

Due to their pore size flexibility, great homogeneity and purity, carbon xerogels can replace activated charcoals in any application requiring texture-tailored and/or very pure carbons. In particular, using a carbon xerogel with an appropriate meso- or macropore size range can eliminate mass transfer diffusional limitations, which are often encountered when the reaction takes place on catalyst supported on activated carbon. Processes traditionally conducted with active carbon supported catalysts could be improved by the use of carbon xerogels with an adequate pore size range. Moreover, the replacement of active carbons by carbon xerogels is realistic because the synthesis process of these materials is extremely simple, reasonably cheap, and easy to transpose to large-scale production.

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