

A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels

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ABSTRACT

The hypothesis about the formation of the porous structure of carbon xerogels when the pH and dilution of the precursor solution are simultaneously modified has been validated by means of scanning electron microscope analysis. The morphology of the carbon xerogels showed that the size and number of the clusters produced during the sol-gel reaction is not only influenced by the pH had but also by the dilution ratio. As with a decrease in the pH value, an increase in the dilution ratio of the precursor solutions caused the formation of a small number of large clusters, leading to materials with large pores. However, depending on the values selected the effect of the pH and dilution ratio was enhanced or diminished by the effect of the other. Hence, an appropriate adjustment of these two variables allowed microporous, micro-mesoporous and micro-macroporous materials to be obtained with pore volumes that could not be achieved by modifying the pH or the dilution ratio separately.

Keywords: carbon xerogels, microwave heating, tailored porosity, scanning electron microscope

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1 Introduction

Carbon xerogels are porous materials obtained by the carbonization of an organic gel [1]. The most frequent organic gel found in the literature is obtained by means of polymerization between resorcinol and formaldehyde in the presence of a solvent [2]. The porous structure and, hence, the final properties of carbon xerogels depends on a large number of variables such as the pH [1-7], type and amount of solvent [5, 8], concentration of reactants [4, 8-10], type of catalyst [1], temperature and time of synthesis [8], carbonization conditions [1], etc. The fact that so many variables modify the properties of these materials is a great advantage since it allows their properties to be tailored to meet the requirements of a specific application.

In the literature, a large number of studies dealing with the effect of different variables (both chemical and physical) on the porous properties of carbon xerogels can be found [1, 8]. However, it is generally accepted that it is the chemical variables that have the greatest influence and, in particular, the concentrations of the reactants (resorcinol, formaldehyde, solvent and catalyst) [4, 10]. The pH, which is determined by the concentration of the catalyst, has been one of the most widely studied variables as it has a great effect upon the porosity of carbon xerogels [1-7]. In general, it can be said that an increase in the pH value favours the addition of formaldehyde to resorcinol anions, leading to the formation of a small number of clusters of reduced size and hence to smaller pores [3, 6]. On the other hand, the dilution ratio, which is commonly defined as the molar ratio between the total solvent and reactants, has an influence on the mechanical strength of carbon xerogels and, accordingly, on the shrinkage that takes place during the drying stage [5]. An increase in the amount of water results in a structure with low mechanical strength which during drying shrinks, leading to a

material with small pores [5]. The effects of these two chemical variables are not isolated and the synergy between them must be taken into account when tailoring the porous properties of carbon xerogels. However, despite the importance of the simultaneous modification of these variables on porosity, few studies in the literature focus on the effect of this synergy. Rey-Raap et al. have highlighted the importance of the synergy between pH and the dilution ratio on organic RF xerogels synthesized by microwave heating [5]. These authors provided a graphic illustration of how the pH and dilution ratio determined the size of the clusters and pores before and after the drying process. Although most studies based on carbon gels indicate that the mesoporosity and macroporosity generated during the synthesis of the organic gel is maintained during carbonization [7], some changes in the size of the clusters and pores can occur due to bonds and individual micropore walls breaking [6] and to the condensation produced during the carbonization process which may cause a slight shrinkage of the polymeric structure [6].

Therefore, in order to achieve total control of the tailoring of the porous structure of carbon xerogels, is worthwhile verifying whether the graphic hypothesis proposed by Rey-Raap et al. [5] for organic xerogels is also applicable to carbon xerogels. Accordingly, the aim of this study is to analyze the morphology of the structure of carbon xerogels synthesized by microwave heating through the simultaneous modification of pH and D in the precursor solution.

2 Experimental

Organic xerogels were synthesized by the polycondensation of resorcinol (R) and formaldehyde (F) using deionized water as solvent and sodium hydroxide as catalyst, following the method described in detail elsewhere [5]. Briefly, resorcinol (Indspec,

99%) was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde (Ercros, 37wt. % in water, stabilized by 10-15% methanol) was added and the mixture was stirred until a homogeneous solution was obtained. Twelve different precursor solutions were prepared with four different initial pHs ranging from 5.0 to 7.0 and three different dilution ratio values (D) ranging from 5.7 to 11.7. All the xerogels were synthesized from 200 ml of precursor solution using the stoichiometric R/F molar ratio (i.e., 0.5).

Once the reactants were selected and mixed in the appropriate proportions, each precursor solution was placed in a microwave oven at 85 °C and kept there for 3 h, which is sufficient time for gelation and curing to be accomplished. After the formation of the polymeric structure excess water was eliminated by continuing to heat the gel in the same microwave oven until a mass loss of over 50% was achieved. The drying step lasted from 1 to 2 hours depending on the pore structure of the material. Carbonization was performed at 700 °C under a nitrogen flow of 150 ml/min in a horizontal tubular furnace. The residence time was 2 hours and the heating rate was set at 50 °C/min. The carbon xerogels obtained were denominated CX followed by the pH value and the value of the dilution ratio.

The porous properties of the carbon xerogels were characterized by nitrogen adsorption-desorption isotherm analysis performed at -196 °C and by means of mercury porosimetry, using a Micromeritics Tristar 3020 instrument and a Micromeritics AutoPore IV, respectively. Before each analysis, all the samples were outgassed at 120°C and 0.1 mbar for 8 h using a Micromeritics VAcPrep 061. These degassing conditions were previously optimized for outgassing this type of material. The

morphology of the carbonaceous structures was examined using a Quanta FEG 650 scanning electron microscope.

3 Results and discussion

The porous structure of the materials studied was analyzed by means of nitrogen adsorption-desorption analysis and the isotherm classification proposed by the IUPAC.

The nitrogen adsorption-desorption isotherms of the carbonized samples are depicted in Figure 1, whilst the pore size distributions obtained by applying mercury porosimetry to some of the carbon xerogels are displayed in Figure 2.

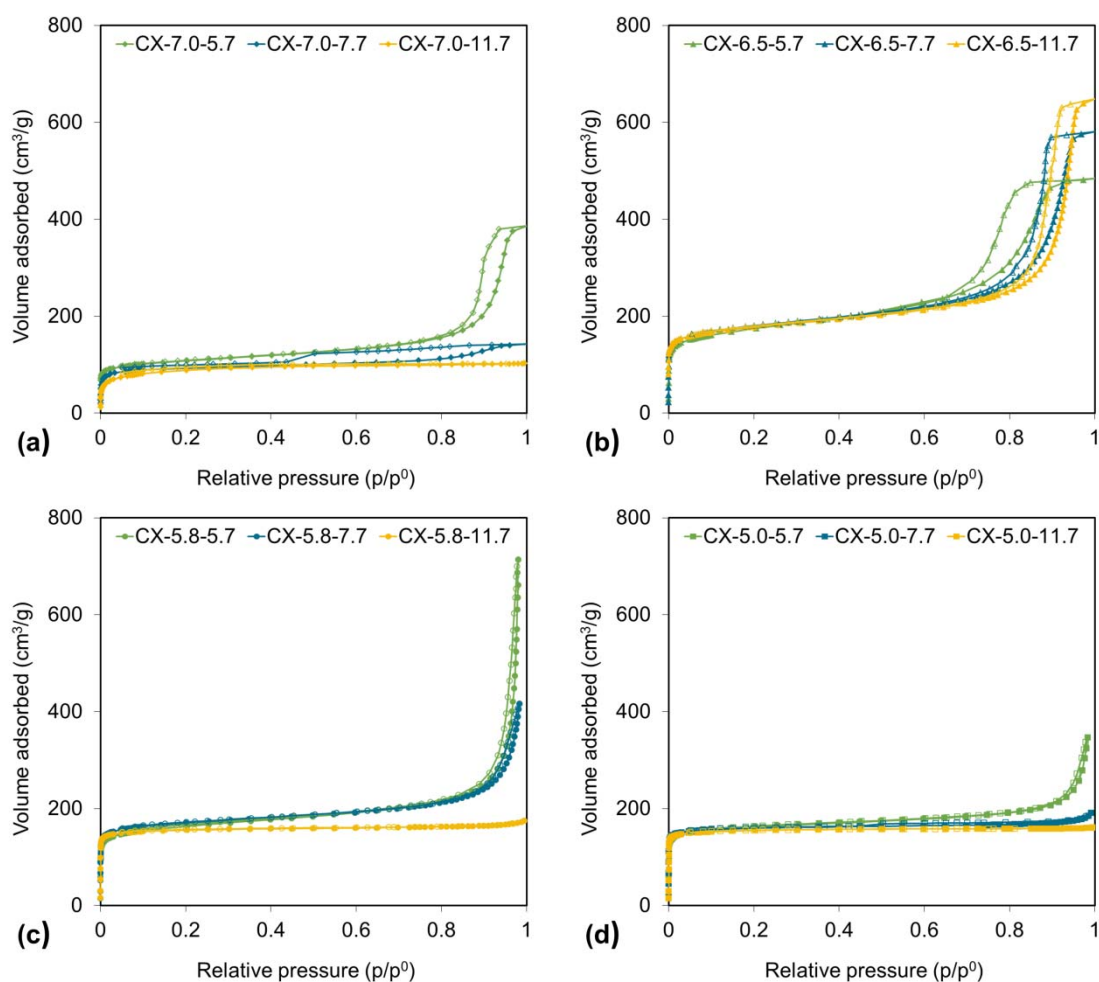


Figure 1. N₂ adsorption-desorption isotherms of carbon xerogels.

The N₂ adsorption-desorption isotherms presented in Figure 1 show a clear difference in shape depending on the pH value of the precursor solution. The influence of the pH on the final properties of carbon xerogels is one of the most studied variables and almost all authors agree about its effect. This effect can be attributed to the two steps involved in the polymerization reaction between resorcinol and formaldehyde: the addition and condensation reactions, as explained in detail elsewhere [5]. Briefly, the catalyst favours the addition reaction, i.e., the formation of resorcinol anions which are the active sites where formaldehyde is added during the addition reaction and where the formation of the clusters starts [19 20]. Accordingly, increasing the pH value of the precursor solution causes the formation of a large number of small clusters interconnected by long necks, resulting in materials with larger pores as shown in Figure 2.

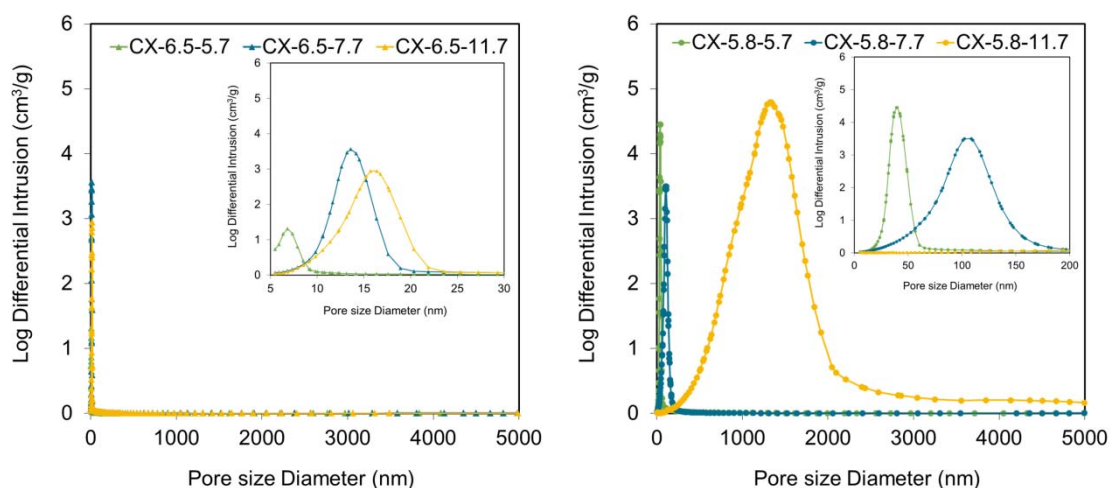


Figure 2. Pore size distribution obtained by mercury porosimetry for carbon xerogels.

In Figure 1 it can also be appreciated that the shape of the isotherm of the samples synthesized from precursor solutions with the same pH value also changes due to the effect of the dilution ratio. Carbon xerogels synthesized from precursor solutions with a pH value of 7 (Figure 1a) evolve from micro-mesoporous materials (combination of isotherm type I and IV) to exclusively microporous materials (isotherm type I) due to an

increase in the dilution ratio from 5.7 to 11.7. Materials obtained from precursor solutions with a pH value of 6.5 lead to isotherms of a combination of type I and IV corresponding to micro-mesoporous materials (Figure 1b). All these samples display a pronounced hysteresis loop associated to the presence of medium-size mesopores. As D increases from 5.7 to 11.7, the hysteresis loop becomes narrower and shifts to higher relative pressures, indicating an increase in the pore size which is confirmed by the pore size distribution in Figure 2a. At lower pH values (Figure 1c and 1d), an increase in D causes the isotherms of the materials to evolve from a combination of type I and II (corresponding to micro-macroporous materials) to type I (corresponding to exclusively microporous materials). However, these carbon xerogels corresponding to a type I isotherm are not exclusively microporous but micro-macroporous materials (Figure 2b). The pore size is large enough to fall exclusively within the macroporosity range and then to become inappreciable when nitrogen adsorption analysis is applied. These results can be clearly appreciated in Table 1 in which the porous properties of the carbon xerogels analysed by mercury porosimetry are listed.

Table 1. Porous properties of carbon xerogels synthesized from precursor solutions with different values of pH and dilution ratio.

Sample	V_{meso} (cm ³ /g)	V_{macro} (cm ³ /g)	d_p (nm)	Porosity (%)
CX-5.0-5.7	0.24	0.92	70	71
CX-5.0-7.7	0.01	2.20	1500	81
CX-5.0-11.7	0.01	2.94	14000	74
CX-5.8-5.7	0.98	0.10	40	69
CX-5.8-7.7	0.13	1.04	100	69
CX-5.8-11.7	0.01	1.87	1200	76
CX-6.5-5.7	0.23	0.00	8	45
CX-6.5-7.7	0.66	0.00	14	59
CX-6.5-11.7	0.67	0.00	18	59
CX-7.0-5.7	0.01	0.00	12	28
CX-7.0-7.7	0.02	0.00	9	25
CX-7.0-11.7	0.03	0.00	9	27

In short, the pore size increases with D provided that the pH value falls below 7. The reason for this effect has not been explained in as much detail as the effect of pH.

However, some authors have reported that an increase in the amount of water leads to a structure with a small number of weakly branched clusters [5, 9]. Depending on the pH (i.e. on the shape and size of the clusters) and because of the vapor-liquid interface generated during drying, shrinkage occurs to a greater or lesser extent and, hence, the porosity of organic xerogels varies. Rey-Raap et al. have provided a graphic illustration of this outcome where it was shown that the number and the size of the clusters was only pH dependent while the degree of shrinkage produced during drying was due to a combination of both the pH and the dilution ratio [5]. These results are in good agreement with the structures shown in Figure 3, where images obtained by applying scanning electron microscopy (SEM) to the synthesized carbon xerogels are presented.

However, some differences can be appreciated between the SEM images obtained in the present study and the graphical hypothesis presented elsewhere (also shown in Figure 3), especially with regard to the shape and size of the clusters.

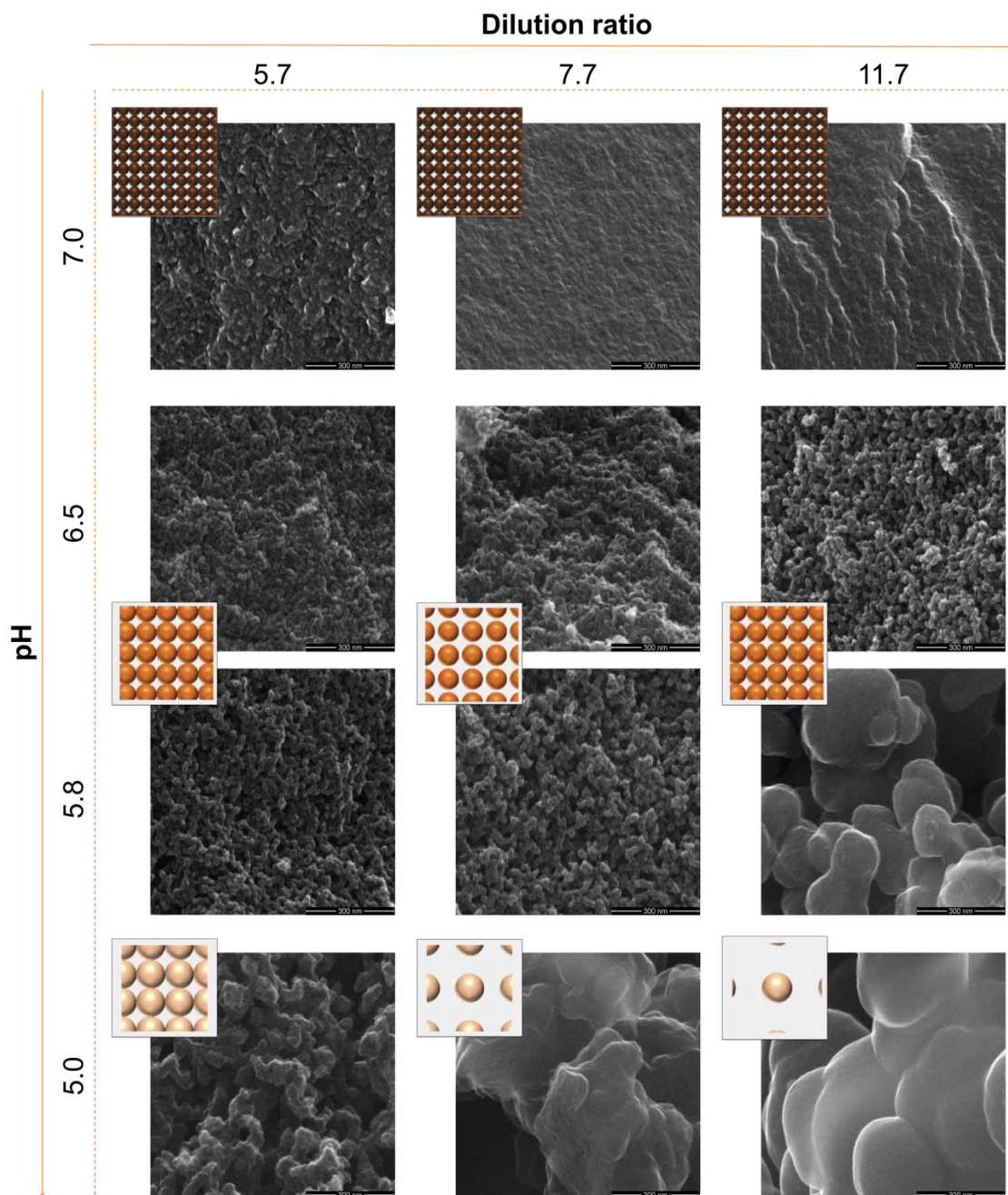


Figure 3. SEM photographs of carbon xerogels.

On the basis of the definition of the dilution ratio and bearing in mind that all materials were prepared using the same volume of precursor, it can be affirmed that high values

of D involve low concentrations of resorcinol and formaldehyde. The lower the concentration of resorcinol, the smaller the number of resorcinol anions generated and, consequently, structures with a reduced number of clusters are formed [10].

Furthermore, the addition reaction takes place more slowly, favoring the condensation reaction and, in this case, clusters of a larger size are formed. Thus, an increase in the dilution ratio gives rise to the formation of larger pores, as previously shown in Figure 2. It should be noted, however, that the pH may increase the effect of the dilution ratio or, conversely, counteract it. That is to say, samples synthesized from a precursor solution with low pH values yield materials with a small number of large clusters.

Furthermore, if the dilution ratio is high (e.g. sample CX 5.0-11.7) the size of the clusters are further increased and the combination of both these effects results in samples with exceptionally large pores (the total pore volume for sample CX-5.0-11.7 was $3.2 \text{ cm}^3/\text{g}$). If both values, the pH and dilution ratio, are low (e.g. sample CX-5.0-5.7), the clusters are large due to the effect of the pH, but of a smaller size than in sample CX-5.0-11.7 due to the effect of the dilution ratio. Thus the effect of one variable counteracts the effect of the other, resulting in a change in the porous structure of the materials, from being macroporous like sample CX-5.8-11.7 to being mesoporous like sample CX-5.8-5.7. Accordingly, in order to tailor the porous properties of carbon xerogels it is necessary not only to control the pH, but also to select the pH value taking into account the concentration of resorcinol and formaldehyde in the precursor solution, i.e., the dilution ratio.

Conclusions

In this study a scanning electron microscope was used in order to validate the combined effect of pH and dilution ratio on the porosity of carbon xerogels. It was found that the

dilution ratio not only had a great influence on the degree of shrinkage but also modified the size and number of the clusters produced during the sol-gel reaction. The results of this study show that high values of dilution ratio give rise to a small number of clusters of large size. This effect is enhanced or diminished by the effect of the pH value of the precursor solution. In this way, microporous, micro-mesoporous and micro-macroporous materials with a large pore volume can be obtained provided that the appropriate pH and dilution ratio values are chosen.

Acknowledgements

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TABLES

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FIGURE CAPTIONS

Figure 1. N₂ adsorption-desorption isotherms of carbon xerogels.

Figure 2. Pore size distribution obtained by mercury porosimetry for carbon xerogels.

Figure 3. SEM photographs of carbon xerogels.

FIGURES

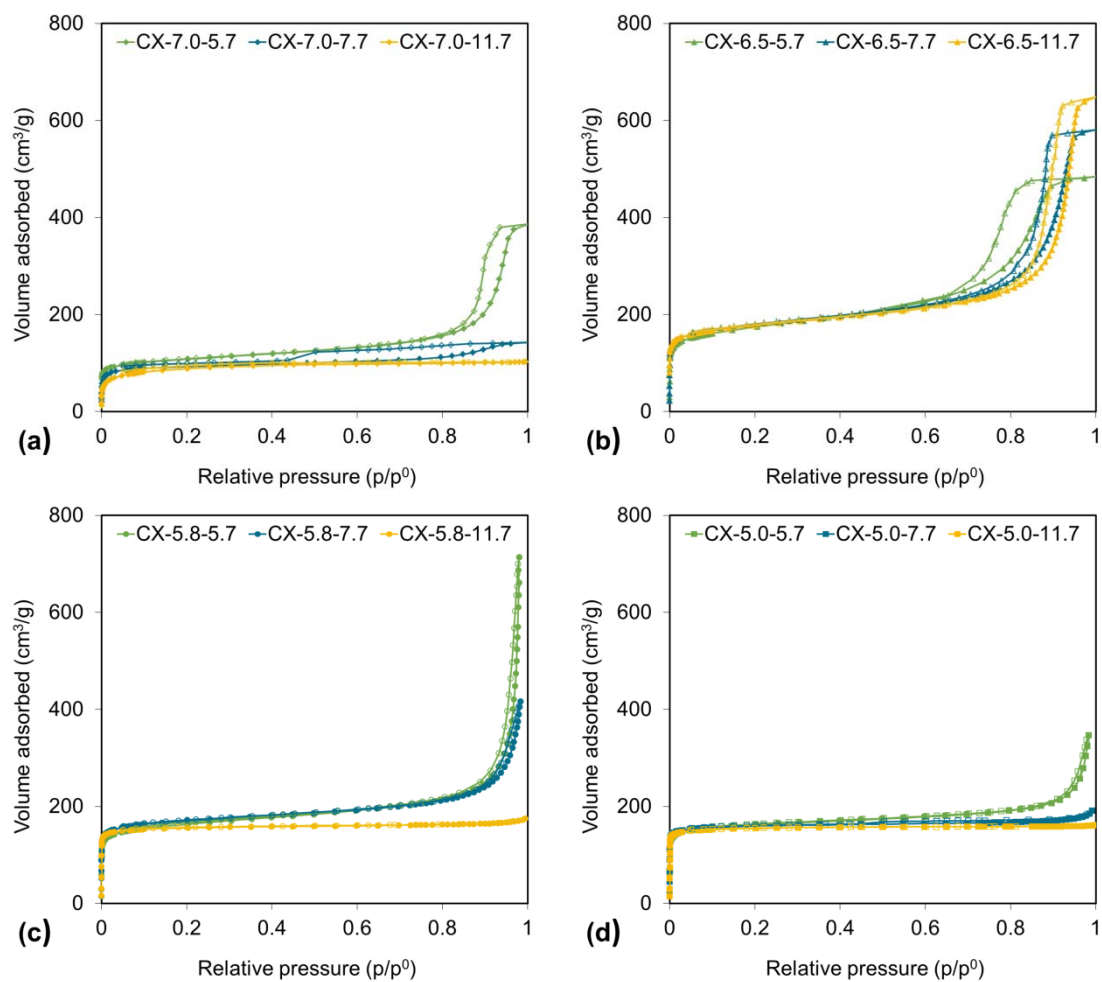


Figure 1

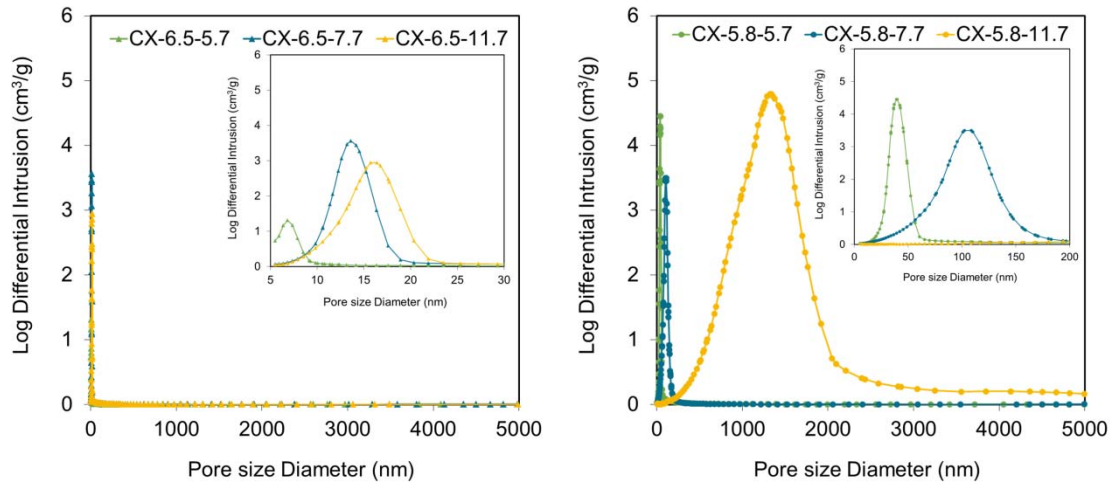


Figure 2

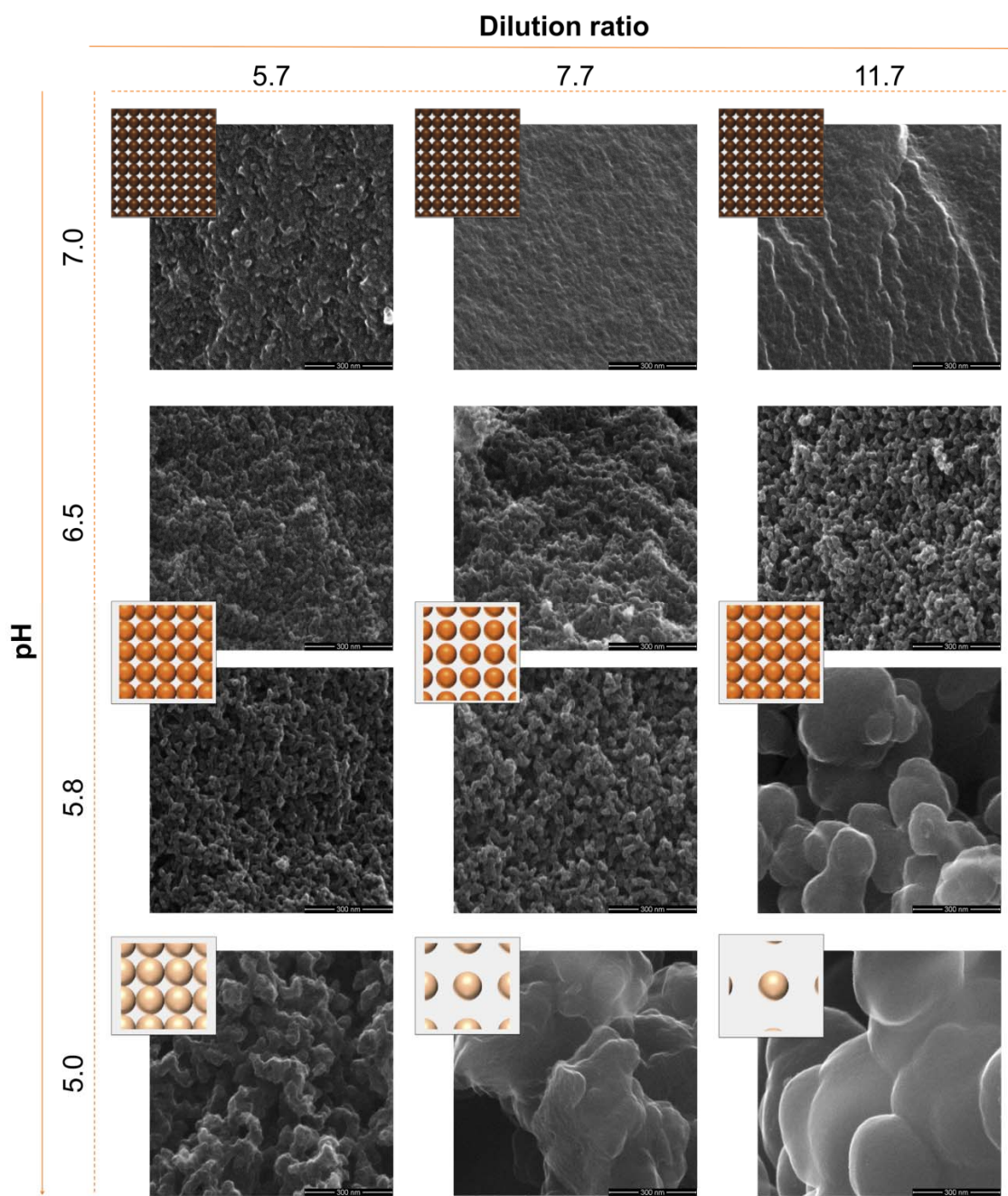


Figure 3