



# Novel synthesis route of metal doped resorcinol–formaldehyde polymer xerogels with tuned porosity



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## ABSTRACT

The complex preparation route of resorcinol–formaldehyde (RF) organogels offers several opportunities for developing metal-containing mesoporous carbon gels. Incorporation of the metal during the sol–gel stage, however, is not always trivial because it can inhibit the polycondensation reaction. A new route is proposed to circumvent this difficulty in the case of molybdenum. We show that a long enough pre-polymerization period (PP) (minimum 110 min in our case) before adding the metal salt yields a mesoporous polymer monolith. Scanning electron microscopy (SEM), low temperature N<sub>2</sub> adsorption and small angle X-ray scattering (SAXS) investigations reveal how changing the PP modifies the structure at various length scales. Adjusting the PP offers a new means of tuning the mesoporosity of the resulting molybdenum-containing RF gels.

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## 1. Introduction

Resorcinol–formaldehyde (RF) gels are the most commonly employed precursors of mesoporous carbon gels. Their versatile synthesis route allows fine-tuning of the pore structure. The literature that addresses the possibility of tailoring the morphology of these gels is abundant (see e.g. [1] and references therein). An additional advantage of the sol–gel preparation method is that it is relatively easy to introduce heteroatoms, e.g. metals, at various stages of the synthesis. This increases the potential of RF and carbon gels in various applications such as catalysis, separation technology or energy storage [2–6]. Several attempts have been made to modify the original synthesis route of Pekala [7] in order to incorporate metals [2–5,8–17]. However, owing to the sensitivity of the catalytic hydrolysis and polycondensation reactions to the experimental conditions, it is a challenge to obtain partial or complete substitution of the alkali-metal salt catalyst without losing the advantages of the RF gel structure.

Molybdenum doping of these gels is of particular interest. Beside their enhanced catalytic activity [3], molybdenum doped carbon aerogels are also very promising candidates as protective gas filters. Chromium impregnation, which was previously widely used in military and industrial gas masks, no longer meets EU standards, owing to the carcinogenic nature of chromium. The chemically

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similar atom molybdenum could potentially replace chromium in these adsorbents. Pérez-Cadenas et al. [18] successfully prepared Mo-doped carbon aerogels, but because of the modified stoichiometry, the resulting samples had only macropores and no mesopores. Maldonado-Hódar et al. recently reported a new preparation method in which surfactants were used to incorporate molybdate anions into the RF hydrogels [19]. The carbon derivatives of their samples, although their pore characteristics and surface area were very limited, showed catalytic activity in the decomposition of isopropanol. For many applications, however, such as gas-filters or catalysts, high surface area with the simultaneous presence of macro-, meso- and micropores is important. Mo-doped carbon aerogels displayed enhanced catalytic activity in the hydroconversion of acetic acid, a model biomass [20,21]. In this work we report a new synthesis route for molybdenum containing RF polymer gels with tunable mesoporosity. As the RF gels preserve their mesopore structure during their conversion to carbon aerogels [22], such polymers may serve as precursors for molybdenum doped carbon aerogels with controlled mesoporosity.

## 2. Experimental

### 2.1. Sample preparation

Molybdenum doped resorcinol–formaldehyde (RF) gels were obtained by a so-called ‘pre-polymerization’ method. The RF sol was prepared as described earlier [22], with the molar ratios of resorcinol (R):formaldehyde (F) 1:2, R: sodium carbonate (C) 50,

resulting a final concentration of 5 w/v% in the aqueous solution. The initial pH of the sol was adjusted to 6.0 with diluted HNO<sub>3</sub>. After 5 min stirring, the beaker containing the RF sol was covered and kept in an oven at 70 °C. After a certain period, referred to as pre-polymerization period (PP, 10–200 min), 10 ml of the RF sol was removed and 0.8 ml of 0.036 M ammonium-heptamolybdate (AM) aqueous solution was added, introducing 1 wt% molybdenum into the gels. The samples were sealed and returned to the oven at 70 °C. After a 7-day curing period the gels were transferred into excess acetone (unless stated otherwise) for 1 day and were dried under ambient conditions until constant mass was attained. All chemicals were obtained from Sigma–Aldrich and used without further treatment.

A blank, Mo-free sample was also prepared by stirring the pre-gelled sample (PP = 200 min) for 1 min, and then incubated for 7 days.

## 2.2. Methods

### 2.2.1. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDX)

Scanning electron micrographs were taken with a LEO 1530 instrument in the ESRF Microimaging Laboratory. Samples were fastened to the sample holder by adhesive carbon tape, and coated with Au to reduce charging.

### 2.2.2. Low temperature nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at –196 °C with a NOVA 2000e (Quantachrome) computer controlled volumetric gas adsorption apparatus. Pre-treatment of the samples was performed at 100 °C at pressure  $P < 3 \times 10^{-4}$  mbar, for 24 h. The apparent surface area ( $S_{\text{BET}}$ ) was calculated using the Brunauer–Emmett–Teller (BET) model [23]. The total pore volume ( $V_{\text{TOT}}$ ) was derived from the amount of vapour adsorbed at relative pressure  $p/p_0 \rightarrow 1$ , assuming that the pores are then filled with liquid adsorbate. The micropore volume ( $W_0$ ) was derived from the Dubinin–Radushkevich (DR) plot [24]. The pore size distribution (PSD) in the micropore region was computed by the Dubinin–Astakhov (DA) method [25], while the mesopore size distribution was calculated from the adsorption branch using the method of Barrett, Joyner and Halenda [26]. Transformation of the primary adsorption data and the (micro)pore analysis were performed by the NOVA2000e Novawin 10.0 software.

### 2.2.3. Small angle X-ray scattering (SAXS)

Small angle X-ray scattering measurements were performed on the ID10A beamline of the European Synchrotron Radiation Facility, Grenoble, France. The collimated and focused 8 keV X-ray beam was directed to the sample by a pair of Si mirrors. To record the scattering patterns a photon counting 2D detector (Medipix [27]) was placed at ~2 m from the sample.

Prior to the measurements the samples were ground to powder, and placed into borosilicate capillaries of diameter 1.5 mm. The capillaries were left at 85 °C for 24 h to eliminate solvent residues. Finally the capillaries were flame sealed to avoid contamination.

The scattering intensities ( $I$ ) were recorded as a function of the transfer wave vector ( $q$ ):

$$q = 4\pi \sin(\theta/2)/\lambda \quad (1)$$

$\theta$  being the scattering angle and  $\lambda$  the wavelength of the incident radiation. As this transfer wave vector is defined in reciprocal space, large  $q$  values correspond to small real distances, and small  $q$  values correspond to large real distances. The distances ( $d$ ) in real space are given by:

$$d = 2\pi/q. \quad (2)$$

Evaluation of the scattering response curves ( $I(q)$ ) was done using the approaches of Guinier and of Porod ( $Iq^4$  vs.  $q$  representation). Details of the calculation are given elsewhere [22]. Briefly, the radius of gyration ( $R_G$ ) of the largest subunits was determined from the Guinier plot  $\log(I(q))$  vs.  $q^2$ .  $R_G$  can be calculated from the region where the Guinier approximation is valid (the smallest  $q$  region), where the slope is  $-R_G^2/3$ . In the Porod plot, given that the samples consist of quasi-spherical subunits, an oscillatory function is present. In this case from the position of the first maximum the radius  $R$  of these spherical subunits can be calculated as  $R = 2.74/q$ .

## 3. Results and discussion

The sol–gel preparation method of RF gels offers an obvious option for metal doping. In general, partial or complete substitution of the catalyst, by a metal salt often yields the desired doped RF gels. Molybdenum, however, is different. Addition of the heptamolybdate salt to the aqueous solution of the monomers promptly induces precipitation: by the end of the reaction a thick, yellow precipitate, poly(molybdic acid), is formed. In Mo-free condition the pH changes continuously as the polymerization progresses [28], while in the presence of the molybdenum salt the pH remains constant, indicating that the polycondensation reaction does not occur. Our hypothesis was that this disadvantageous situation might be overcome if the molybdenum salt is added to a partially consolidated RF network. A pre-polymerization period (PP) was therefore employed and the molybdenum was added to the pre-gelled RF system. During this period the RF gel network becomes firmer and the destructive effect of the molybdenum is less severe. Here we present a systematic study of this preparation method for Mo-doped RF gels. Our aim was to reveal the optimum conditions of molybdenum doping, and to find a compromise between the duration of the PP (and thus the strength of the RF gel) and the porous structure of the resulting doped RF gels.

The macroscopic appearance of the samples obtained after the 7-day curing period differed greatly. Because no sign of gelation was observed in samples with PP < 60 min, these were not investigated further. When the AM solution was added after 70–80 min, traces of the yellow precipitate still remained in the samples, but they were very finely distributed: the samples were turbid but apparently homogenous. For PP  $\geq$  80 min, addition of the AM solution instantaneously transformed the RF sol into a pale brown, viscous liquid. Uniform, gel-like samples were obtained only after PP > 110 min. The molybdenum was not incorporated chemically into the gel, because the Mo appeared in the washing solvent as isopoly molybdenum blue anion [29]. For shorter values of PP the samples obtained were powders with a grain size that depended on PP. On microscopic length scales the change in the structure is illustrated in Fig. 1 by the SEM images of the dry xerogels.

The yellow poly(molybdic acid) precipitate obtained with PP = 60 min consists of large separate beads. The bead size of the sample dried from acetone is 4–10  $\mu\text{m}$  (Fig. 1a, left). The diameter of the beads dried after washing in water shrank by about 50% (Fig. 1a, right), possibly due to the higher surface tension of water. As PP increases, the structure gets finer and the size of the subunits decreases. The PP = 80 sample – as also observed macroscopically – represents an intermediate state (Fig. 1b). This kind of transition structure was already reported by Pérez-Cadenas et al. [18]. The network of the smaller RF spheres is apparent but the larger single beads of the poly(molybdic acid) are still present. Their size however is much smaller than in the PP = 60 min sample (1–2  $\mu\text{m}$ ). In samples with even longer PP only the small spherical units of the RF network are visible and the structure becomes increasingly compact. The shrinkage effect of the washing solvent vanishes as

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