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Predicting the suitability of aqueous solutions of deep eutectic solvents for preparation of co-continuous porous carbons via spinodal decomposition processes

E. Posada [a], N. López-Salas [a], D. Carriazo [a, b, c], M.A. Muñoz-Márquez [b], C.O. Ania [d], R.J. Jiménez-Riobóo [a], M.C. Gutiérrez [a], M.L. Ferrer [a, **], F. del Monte [a, *]

[a] Materials Science Factory, Instituto de Ciencia de Materiales de Madrid-ICMM, Consejo Superior de Investigaciones Científicas-CSIC, Campus de Cantoblanco, 28049, Madrid, Spain
[b] CIC Energigune, Parque Tecnológico de Alava, 01510, Miñano, Spain
[c] Ikerbasque, Basque Foundation for Science, 48011, Bilbao, Spain
[d] Instituto Nacional del Carbon-INCAR, Consejo Superior de Investigaciones Científicas-CSIC, C/Francisco Pintado Fe 26, 33011, Oviedo, Asturias, Spain

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ABSTRACT

Spinodal decomposition (SD) processes have proved effective for the synthesis of macro- and mesoporous materials. Despite the theoretical aspects of SD processes are well understood, finding the proper experimental conditions – both the components as well as the ratio in which they have to be combined – to attain co-continuous structures is a non-predictable and quite tedious process, typically based on trial and error. The challenge is finding a "tool" capable to predict the suitability of a particular starting solution to undergo SD processes. Here in, we used aqueous solutions of deep eutectic solvents (DESs) for the preparation via SD of co-continuous porous carbons, the morphologies of which ranged from spinodal to aggregates-of-particles-like just depending on dilution. Despite the starting DES/H_2O binary mixture was macroscopically homogeneous, Brillouin spectroscopy revealed the occurrence of certain nanostructural rearrangements within a dilution range that coincided with that used for preparation of carbons with morphologies transitioning from spinodal to aggregates-of-particles-like. Moreover, carbons exhibited a noticeable degree of heteroatom co-doping – e.g. N and P – and proved particularly effective for CO_2 capture with adsorptions of up to 4.7 mmol/g at 0 °C and 760 mbar.

1. Introduction

Porous carbons are lately attracting considerable attention due to their potential in applications such as membranes for adsorption, filtration and separation [1], catalytic supports [2], electrodes in fuel cells, supercapacitors or batteries [3–5], or controlled release media [6], among others. In practical terms, hierarchical materials combining small and large pores are required. It is well known that the former are the main responsible of the activity – the larger the surface area, the higher the activity – but it is also worth noting that the ultimate performance of these materials is largely dependent on the accessibility to such an active surface. Thus, efforts must focus on the design of synthetic processes promoting the formation of co-continuous structures of interconnected pores with mean diameters in the nano/micrometer range that allow mass transport throughout the whole three-dimensional structure.

A number of synthetic routes have been explored by using different carbonaceous precursors [7,8] and either hard or soft templates to modulate the porous texture of the resulting carbon structures [9,10]. In this regard, syntheses using hard-templates – where the pore structure is a replica of pre-synthesized mesoporous oxides and nanoparticles – typically suffer from a tedious procedure during the preparation and removal of templates – e.g. chemical etching. Thus, syntheses based on the use of soft-templates – via self-assembly of carbon precursors with block copolymers and surfactants that are sacrificed as porogens during carbonization – are considered as a more convenient approach. In this latter case, microphase separation induced by the well-ordered phases of self-assembled block copolymers and surfactants are

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* Corresponding author.
** Corresponding author.
E-mail addresses: mferrer@icmm.csic.es (M.L. Ferrer), delmonte@icmm.csic.es (F. Monte).

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responsible of the ultimate structure of the resulting materials. Nonetheless, the scale-up capability of these soft-template syntheses is questionable because the synthetic origin of most of block copolymers and surfactants make them costly and non-friendly in environmental terms.

Within this context, more environmentally benign and cost-effective phase-separation processes have been investigated. Among others, spinodal decomposition (SD) processes have proved effective for the synthesis of macro- and mesoporous materials [11–16]. In this case, it is widely accepted that phase separations can be induced both thermally and chemically. Thermally induced phase separations are applied when the phase diagram of a certain polymer exhibits an upper critical solution temperature so that a homogeneous solution formed at a determined temperature is phase separated by thermal quenching. In chemically induced phase separations, the growth of oligomers/polymers makes them less and less soluble in the originally homogeneous starting solution and results in a phase separation – i.e. between a polymer-rich and a polymer-depleted phase – that is ultimately frozen upon gelation when the growing polymers reach a certain degree of cross-linking. Diverse structures – e.g. interconnected or open-cell pores – can be formed depending on the experimental parameters used for polymerization such as the solvent of choice and its volume fraction, and/or the temperature. Nonetheless, the transient structure that results from phase separation comes ultimately determined by the time relation between the onset of phase separation and gel formation – e.g. interconnected structures with a network-like morphology if the onset of both processes coincides, or with an aggregates-of-particles morphology if phase separation occurs earlier than gel formation so that the polymer-rich domains break-up and become spherical during the coarsening process of the SD in order to decrease the interfacial energy [17–19].

SD processes have been typically used for the preparation of porous metal oxides via sol-gel [17,18,20–31], vinyl and acrylate polymers via radical polymerization [32–44], and epoxy, phenolic and furfuryl resins via condensation (Table S1) [45–60]. It is worth noting that submission of some of these polymers – e.g. vinyl polymers as well as phenolic and furfuryl resins – to a carbonization process is a common process to obtain macroporous carbons [38–40,50–60].

In practical terms, the achievement of co-continuous structures via SD processes need of homogeneous starting solutions containing (1) the monomers/precursors that will form the final polymer/material and (2) a phase-separation-inducing agent – PSIA – that, at a certain stage of the process, segregates from the originally homogenous solution into a continuous phase. Eventually, the starting solution also contains (3) a co-solvent that helps to demix the PSIA and the growing polymer into a co-continuous-phase-separated system. The PSIA most widely used – either by its own or with the aid of some additional co-solvents – with every of the monomers/precursors has been polyethylene glycol (PEG) but the use of other polymers is also common – see, for instance, propylene oxide (PO), polypropylene carbonate (PC), polydimethylsiloxane (PDMS), or polyacrylamide (PAAm) in Table S1. In these cases, both the polymer mass ratio – referred to the monomer/precursor – and the molecular weight have been used to control the SD process and thus obtain different morphologies. More recently, co-continuous structures via SD processes have been obtained using different mass fractions of single co-solvents – e.g. formamide, ethyleneglycol, ethanol, or even water in some few cases – as PSIAs (see Table S1). Despite the theoretical aspects of SD processes are well understood, finding the proper experimental conditions – both the components as well as the ratio in which they have to combine among – to attain co-continuous structures via SD processes is a non-predictable and quite tedious process, typically based on trial and error. Thus, finding a "tool" capable to predict the suitability of a particular starting solution would indeed be challenging. For this purpose, we hypothesized that a simplification of the starting solutions by using single co-solvents as PSIAs – e.g. those described above or, at least, similar to – would be also of help to get the rationale behind the experimental aspects of the process.

Our group has recently reported on the preparation of co-continuous porous carbons using deep eutectic solvents (DESs) [61–65]. DESs were first described by Abbot and coworkers in 2003 [66] as supramolecular complexes formed between an hydrogen bond donor – HBD – and an hydrogen bond acceptor – HBA, typically an ammonium or phosphonium salt. More recently, similar eutectics have also received the name of low-melting eutectic mixtures – by König and coworkers [67] – or low-transition–temperature mixtures – by Kroon and coworkers [68]. DESs share many characteristics with conventional ionic liquids (ILs) – e.g. non-reactive with water, non-volatile, and biodegradable – but the decrease in the melting point in DESs is ascribed to the charge delocalization that occurs between the HDB and the HBA. In our case, DESs were composed of phenol derivatives and ammonium salts, so that the materials resulting after polycondensation exhibited a co-continuous porous structure obtained via a SD process where the formation of a polymer-rich phase by polycondensation was accompanied by the segregation of the non-condensed matter – e.g. the ammonium salts – creating first a polymer-poor phase that, ultimately, becomes a polymer-depleted phase [69–72]. We found that this phase-separation process ends with the formation of either interconnected or aggregates-of-particles-like structures but, despite we have been recently capable to tailor the textural properties of the resulting porous carbons [73], we never rationalized the experimental conditions that let transitioning from one structure to another.

Herein, we demonstrate how carbons prepared from DESs could exhibit different morphologies upon the control of the SD process. The DES of choice was based on a mixture of resorcinol, glycerol, phosphoric acid and choline chloride in a 1:1:1:1 molar ratio, being studied by ^{1}H NMR spectroscopy and differential scanning calorimetry (DSC). This DES was used for the preparation of porous carbons via polycondensation with formaldehyde, and subsequent carbonization. The degree of condensation of the polymers resulting after polycondensation was studied by ^{13}C NMR and FTIR spectroscopies. The morphology of the resulting materials was studied by scanning electron microscopy. As mentioned above, SD processes typically need of a PSIA that, at a certain stage of the process, segregates from the originally homogenous solution into a continuous phase. In our case, we just used water as co-solvent and different mass fractions of it – i.e. first, that originally coming from the formaldehyde solution and then, increasing this one upon further additions – to tailor the morphology of the resulting co-continuous structure. Thus, we also studied the starting DES/H_2O binary mixtures by Brillouin and ^{1}H NMR spectroscopy to better understand the rationale behind the SD process. On the basis of these results, we finally proposed a mechanism for DES-assisted SD processes alternative to that widely accepted for regular ones. Finally, insights about the textural properties of the resulting carbons were obtained from N_2 and CO_2 adsorption/desorption isotherms, and Hg porosimetry. The resulting N,P-doped carbons exhibited an outstanding performance when we studied their CO_2 adsorption capabilities at 760 mbar and at 0 and 25 °C.

2. Experimental

2.1. Materials

Resorcinol (R), phosphoric acid (P), glycerol (G), choline chloride