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A REVIEW: THE INFLUENCE OF THE CATALYST ON FORMATION AND PROPERTIES OF RESORCINOL--FORMALDEHYDE GELS

PRZEGLĄD: WPŁYW KATALIZATORA NA POWSTAWANIE ORAZ WŁAŚCIWOŚCI ŻELI REZORCYNOWO--FORMALDEHYDOWYCH

Abstract

The paper summarises the findings of the most significant studies on the effect that the catalyst has on the formation and properties of organic gels, synthesised *via* the sol-gel method from resorcinol and formaldehyde. These materials exhibit excellent electrical and mechanical properties, as well as have great specific surface areas, and thus are excellent materials for manufacturing electrodes in a variety of appliances, from rechargeable batteries to supercapacitors. The properties of these gels can be adjusted to meet the desired values, however, they are controlled by a number of factors. The most interesting of these is the catalyst and its role, as it is elusive and has been investigated only by several authors across the globe.

Keywords: organic gels, organic aerogels, catalyst, formaldehyde, resorcinol

Streszczenie

W artykule streszczono wyniki najistotniejszych prac naukowych poświęconych wpływowi katalizatora na powstawanie oraz właściwości końcowe żeli organicznych, otrzymywanych metodą zol-żelową z rezorcyny i formaldehydu. Materiały te posiadają doskonałe właściwości elektryczne i mechaniczne, a także posiadają duże wartości powierzchni właściwych, przez co są doskonałymi materiałami do produkcji elektrod w różnych urządzeniach, począwszy od akumulatorów aż po superkondensatory. Właściwości tych żeli mogą być dostosowane do oczekiwanych wartości, jednakże są one też kontrolowane przez wiele czynników. Najbardziej interesującym z nich jest katalizator oraz jego rola, ponieważ jest ona niejasna i była zbadana zaledwie przez kilkoro naukowców na świecie.

Słowa kluczowe: żele organiczne, aerożele organiczne, katalizator, formaldehyd, rezorcyna

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1. Introduction

Organic aerogels were first synthesised using the sol-gel technology by R. W. Pekala in 1989, at the Lawrence Livermore National Laboratories in the USA [1]. Since then, they have gained international interest and became the focus of research in the broad field of energy-related materials. The precursors of these materials are organic wet gels, synthesised in aqueous solutions of resorcinol and formaldehyde, in the presence of a basic catalyst, such as sodium carbonate, sodium and potassium hydroxides. The reaction follows a general path shown in Fig. 1.
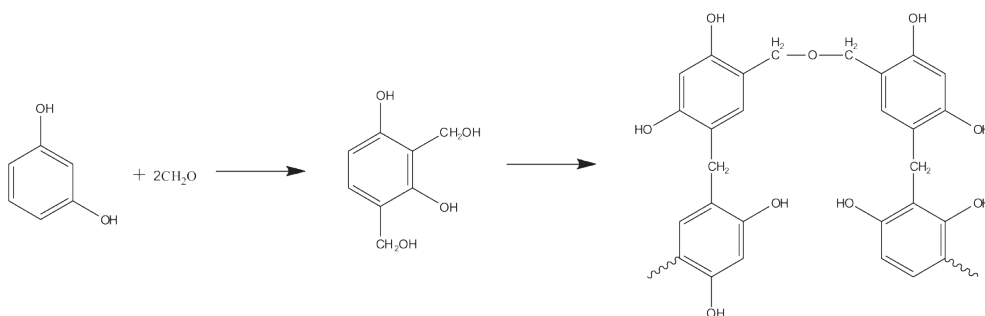

Fig. 1. Overall path of resorcinol and formaldehyde reactions in aqueous solutions, leading to the formation of resorcinol-formaldehyde gels

These aerogels are characterised by very high porosity, and thus high surface area, reaching several hundreds of square metres per gram. Their most interesting feature is their excellent electrical properties, such as capacity and conductivity. Owing to these properties, they are ideal materials for the construction of electrodes in a variety of appliances, such as batteries, rechargeable batteries and supercapacitors [2–4].

The sol-gel process, in which their precursors are obtained, is controlled by a number of factors, such as temperature, concentration of reagents – both total and relative – and concentration of catalyst and its type. It is also probable that the duration of the process and stirring also have an effect on the physical mechanism of the gel synthesis, and thus the final properties of the resulting gel.

2. Influence of the initial pH on the properties of the resulting gel

Several key issues need to be taken into account when investigating the influence of the catalyst on the porous properties of an organic gel. The main role of the catalyst, in this particular case, is providing the most favourable conditions for the reaction between resorcinol and formaldehyde. In practice, this means adjusting the pH to the desired level, and thus enabling the reaction. Later on, the chosen pH value can affect the whole process. The catalyst type needs to be chosen appropriately, along with its concentration.

The most commonly used catalysts chosen for the synthesis of resorcinol-formaldehyde gels are those, which provide an alkaline solution upon dissolution in water. The very first studies [1] proved that the gels, with arbitrarily named best properties, are those synthesised at pH above 6.0, however, the study did not cover solutions with initial pH values above 7.5. Some of the later studies [5, 6] also did not include these, however, a couple of studies [7, 8] also included experiments in which the initial pH was as high as 9.0. The overall conclusions drawn from these studies were that gels could not be obtained from solutions with an initial pH below 6.0, and instead, the solutions became opaque or a precipitate formed after heating. Interestingly, when the initial pH was above 8.0, the gel also did not form according to one study [7] or it contained virtually no pores, according to another study [8]. Research carried out by Lin et al. [5] proved that carbon xerogels synthesised with an initial pH in the range of 7.0–7.5, and were virtually solid with no pores. Only when the pH was decreased by the addition of nitric acid, both the pore volume and the surface area increased, which is natural as these are related to each other. The most significant increase, from 0 to 600 $m^2 \cdot g^{-1}$, was observed for samples with the initial pH decreased with addition of nitric acid, from 7.0 to 6.5. Moreover, the results of this study have shown that the pore volume increased linearly with the decrease of pH in the range of 7.0–5.7. Moreover, findings of Lin et al. [5] also included the fact that the lower the initial pH, the broader the pore size distribution, therefore, a more uniform structure could be obtained from solutions with pH closer to 7.0. Results of Zanto et al. [9] appear to confirm these findings, underlining that the most significant factor affecting the surface area and pore volume is the initial pH, and not the weight percentage of solids, a measure chosen by some as a factor determining the final properties of gel. Nevertheless, it is worth reminding that the pH is strictly connected to the concentration of the catalyst, which is typically added at a given molar ratio to resorcinol, which is in turn at a fixed molar ratio with formaldehyde.

Research done by Job et al. [6] confirmed an assumption arising from previous literature that the specific surface area can be adjusted by varying the initial pH value. An increase of pH from 5.45 to 7.35 caused the specific surface area to increase from 330 $m^2 \cdot g^{-1}$ to 470 $m^2 \cdot g^{-1}$, however, a maximum of 510 $m^2 \cdot g^{-1}$ was found at pH equal to 6.50. Therefore, this study confirms that the relationship between the initial pH and the surface area is not linear in the range of 5.45 to 7.35. Similarly, a more recent study by Zubizarreta et al. [8] focused on the influence of the initial pH on the surface area of resorcinol-formaldehyde gels. The main conclusion arising from this paper is that the highest surface area can be achieved when the initial pH was between 6 and 7, and that it is much higher than of those synthesised at pH equal to 9.

Several researchers [10, 11] investigated the use of acidifying agents (acetic acid) as catalysts. These studies successfully covered pH range lower than 5.0 and proved that gels can also be formed in such conditions. Nevertheless, their porous properties are different than of those synthesised using basic catalysts. Moreover, they strongly depend on the chosen resorcinol to catalyst molar ratio (R/C). For instance, only a very weak relationship between the pore size and the R/C ratio was found, while for basic-catalysed gels this relationship is strong. Nevertheless, at very high R/C ratios (above 1000), both acid- and base-catalysed resorcinol- formaldehyde gels have almost the same properties, as far as electrical conductivity, elastic moduli, micropore size and volume are concerned [11].

3. Influence of the catalyst type on the properties of the resulting gel

As it appears from the published results of numerous studies, not only the pH of the initial solution influences the properties of the resulting material, but also the chemical compound used as a catalyst. The most often chosen catalysts are alkaline because the preferred reaction conditions are mildly basic, while both resorcinol and formaldehyde produce an acidic environment upon dissolution in water. Most researchers use the same catalyst as Pekala did in 1989 and afterwards [1, 12, 13], i.e. sodium carbonate. This compound does not cause difficulties in handling and storing, it is relatively safe, easily available and inexpensive, hence its popularity [2, 14–19]. Nonetheless, other basifying agents were investigated, such as sodium and potassium hydrogencarbonates [20, 21] and potassium carbonate [21, 22]. Alkaline hydroxides are also popular with researchers – hydroxides of sodium, potassium, lithium, calcium, barium, magnesium and strontium were extensively studied [20, 23]. The prevailing hypothesis states that the primary role of the catalyst is to provide an appropriate pH, therefore, even ammonia was studied as a potential catalyst [20], however, with little success. Tamon et al. [20] proved that the alkaline metal cation is necessary for the synthesis and gel formation, as ammonia failed to successfully catalyse the reaction.

Fairen-Jimenez et al. [22] found that for the same concentration of the reactants, i.e. formaldehyde and resorcinol, gels produced with sodium carbonate were denser than those synthesised with potassium carbonate as the catalyst. They also had smaller a pore volume and smaller pore diameters. This study was followed by a far more extensive one by Job et al. [23], in which alkali metal hydroxides and alkali earth metal hydroxides were examined, leading to a conclusion on the influence of the type of metal on the synthesis process. The results showed that the size of the metal cation does not influence the pore characteristics of the resulting gel, however, its charge and concentration do. Alkali earth metals (charge +2) led to gels with larger pore sizes than those synthesised in the presence of alkali metals (charge +1). The initial pH was kept constant, meaning that the concentration of alkali metal hydroxides was roughly twice the concentration of alkali earth metal hydroxides. The explanation for this effect provided by Job et al. binds the effect of ions on the pore structure with electrostatic effects on the microphase separation process prior to the gelation. It is known that salts destabilise colloidal suspensions and may lead to their coagulation and Job et al. claim that this is what controls the gelation step. The repulsion between colloidal particles is screened over the Debye–Hückel distance, which is inversely proportional to $\sqrt{\sum nq^2}$,

where n is the concentration of ions and q is their charge. Therefore, earth metal cations with a + 2 charge are more effective in screening these repulsive forces, leading to a destabilisation of the suspension and gel formation at an earlier stage of the reaction. As a consequence, the obtained gels have larger pores, even when the same initial pH was provided.

Findings of Job et al. [23] were mostly in agreement with findings of a more recent study by Morales-Torres et al. [16], in which five alkali carbonates were used as catalysts (Li, Na, K, Rb, Cs). The results showed a relationship between the size of the counter-ion and the gelation time. Moreover, the slower the gelation, the larger the primary particles, therefore, also larger pores. In their study, Morales-Torres et al. suggest that the growth of the resorcinol- formaldehyde gels takes place via the formation of anionic species induced

by the catalyst. Therefore, electrostatic interactions are present, and thus it might be worth to consider the application of surfactants in order to provide a better control over the process.

A study on acid-catalysed sol-gel process of resorcinol-formaldehyde gels synthesis in aqueous solutions was done by Brandt et al. [11]. The study observed that the greater the concentration of the catalyst – acetic acid – the smaller the particles that form the gel network. At the same time, the dependence of the pore sizes of the gel on the R/C ratio is much weaker than for gels synthesised using basic agents, as it was previously mentioned in this paper.

Mulik et al. [10] performed a study in which resorcinol-formaldehyde gels were synthesised using hydrochloric acid as catalyst and acetonitrile as solvent. Even though two factors were altered – solvent type and catalyst – the results showed that these gels were virtually indistinguishable by IR and ^{13}C CPMAS NMR from the base-catalysed materials. Mulik et al. reason that the acid-catalysed route to gel formation is acceleration of the reaction *via* increasing the positive charge of the electrophile rather than the activation of the aromatic ring by enhancing the ability to donate electrons of the substituents (OH to O-), as it is in case of the base-catalysed synthesis. On the other hand, results provided by Fairen-Jimenez et al. [22], before Mulik et al. study, proved that the acidic catalyst affected only the gelation process. This study [22] also proved that when using acidic catalyst, oxalic acid or para-toluenesulfonic acid, the density of the resulting material is greater than in the case of alkaline carbonate catalysts by a factor of two or even three, suggesting that the use of acidic catalyst greatly enhances cross-linking and condensation.

A number of studies revealed a dependence of the porous properties of the resorcinol-formaldehyde gels on the concentration of the catalyst. In most cases, the catalyst influence is examined not as an absolute concentration, but as a relative measure – the resorcinol-to-catalyst molar ratio.

There is a large number of studies, which handle the effect of the R/C ratio on the properties of the final material, but they are mostly consistent in their findings. A study performed by Saliger et al. [24] showed that the growth of particles forming the gel could be controlled by the concentration of the catalyst, appropriate concentration of the reactants and the temperature. The amount of catalyst was claimed to control the size of the particles constituting the gel network, under the assumption that more catalyst translates into more numerous active sites in which these particles are formed, leading to structures with smaller particles, and thus pores. Interestingly, Saliger et al. managed to obtain materials with cluster sizes in the μm range, while typically, particles of a nanometre scale are observed. Findings of Saliger et al. were confirmed by findings of Bock et al. [25], who found that for lower R/C ratios (i.e. higher catalyst concentrations), the gel structures were finer, which corresponds to smaller primary particles.

A review by Al-Muhtaseb et al. [3] summarises some research findings on the resorcinol-formaldehyde gels. The overall conclusion is that the structure of gels synthesised in the presence of a low concentration of catalyst (i.e. high R/C ratio) resembles "string-of-pearls". This means that there is a number of rather large (16–200 nm in diameter) particles connected with thin strings. This is not the case for materials that are more fibrous in appearance, obtained in conditions of a high catalyst concentration. In that case, the diameter of the particles and the links between them is virtually the same and varies around much smaller values of only 3–5 nm. The reasoning behind this finding is that a lower catalyst concentration allows longer growth of the primary particles prior to gel the formation. As a result, the pore sizes are greater.

A study by Job et al. [6] is in agreement with these findings and attempts to provide an explanation for this phenomenon. When high concentration of catalyst is used, the rate of hydroxymethyl derivatives formation, as well as the extent of substitution, are high. As a result, highly-branched clusters are formed. These structures condense readily, therefore, they do not remain in the nucleation regime for long, and thus, form smaller clusters. When a low concentration of catalyst is used, the effect is contrary: lowly-branched structures are formed and they persist in the nucleation regime for a longer period of time, allowing growth without condensation and gelation.

A significant majority of the available studies focus on the influence of the R/C ratio on the resulting properties of the gel, and not directly on the mechanism itself. Only some attempted at explaining the role of the catalyst by correlating the final properties with the reaction conditions. Nevertheless, a direct observation would be far more valuable. There is a very limited number of such studies using Dynamic Light Scattering (DLS) to examine the changes caused by altering the R/C ratio, or the catalyst type, on the gelation mechanism. One of the studies was done by Berthon et al. [15], who mostly studied the influence of the solvent and the type of catalyst on the gels. While the authors dedicated a significant amount of research to the non-aqueous reacting solutions, only one R/C ratio of aqueous solution was investigated. Nonetheless, the study suggested that the mechanism of gel formation is different for acid and base-catalysed syntheses. A far more relevant study was conducted by Yamamoto et al. [17], in which DLS experiments were carried out on samples with a varying catalyst (sodium carbonate) and resorcinol concentrations. The main findings of this study are that the growth rate of the primary particles depends on the catalyst and resorcinol concentrations. Moreover, this relationship is not linear throughout the whole synthesis process. Yamamoto et al. [17] also found that as the reaction reaches approximate gelation time, the shape of the decay time spectrum becomes bimodal, indicating the formation of a less-mobile structure, probably the gel network. The most recent study by Gaca et al. [18] employed DLS to examine the influence of the R/C ratio on the growth rate of primary particles, namely agglomerates of hydroxymethyl resorcinol derivatives, at two different temperatures. The results indicated that the size of primary clusters forming the gel network appears to be thermodynamically controlled and the miscibility limit is reached upon the formation of reaction intermediates, which most likely are relatively small. This results in nanoscale molecular demixing, leading to the formation of monodisperse primary clusters. At higher catalyst or reactant concentrations, more numerous primary clusters are produced due to faster reactions. Authors believe that the primary clusters may be initially liquid-like, and further polymerisation may proceed faster within them than in the bulk solution due to locally higher concentrations of intermediates. The overall conclusion of these papers is that the process appears to be far more complex than previously assumed.

4. Conclusions

As numerous studies have shown, the catalyst plays a decisive role in the synthesis of resorcinol-formaldehyde gels. Its role is complex and appears to be of both physical and chemical nature. Not only does its concentration has an effect, but also its type. Moreover, its influence can be synergistic with other factors, such as concentration of the reactants.

The effect of the R/C ratio on the surface area is significant, however, it varies across studies. In many cases, a maximum value was found for certain conditions and it appears that more factors than just R/C ratio determined this. It also seems that the pH is a more influential factor than the R/C ratio, though these two are connected.

A lack of thorough studies on the influence of the catalyst, its type and concentration is seen in the literature. Only a couple of papers cover this matter, while it appears to be crucial in determining the actual role played by the catalyst in the sol-gel process.

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