IRSTI 31.25.01 https://doi.org/10.26577/IJBCh202518213

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(Received 15 December 2025; received in revised form 23 December 2025; accepted 25 December 2025)

Acid- and amide-controlled sol–gel synthesis of SiO_2-based polymer composites

Abstract. The sol–gel method is a versatile approach for synthesizing advanced inorganic and organic–inorganic hybrid materials with controlled structure, high purity, and tunable functionality. This study systematically investigated the hydrolytic polycondensation of tetramethoxysilane under acidic conditions to develop an optimized route for high-quality SiO_2-based polymer–inorganic composites. The effects of medium acidity, catalyst type, solvent, and amide-based drying-control chemical additives (DCCA) on hydrolysis and condensation kinetics were evaluated. Strong acids accelerated hydrolysis, while weak acids promoted gradual condensation, yielding highly porous but mechanically weaker gels. Acetic acid facilitated homogeneous gel formation and improved transparency and pore uniformity by removing volatile ester by-products. Among the amides, dimethylacetamide and diethylformamide were found to be effective pH regulators in gelation, yielding dense, crack-free gels with lower microporosity and improved mechanical strength. SEM investigations have confirmed the more homogeneous, more compact structures of dimethylacetamide-containting gels, as compared with amide-free gels. Use of acetic acid as the solvent played an important role in controlling the micro-pores, carbon content, density, and stability of gels. In general, this work presents a comprehensive methodological approach for designing sol–gel SiO_2-based hybrid nanomaterials with designed structural and physicochemical properties, with their potential use in advanced optical, catalysis, coatings, and other functional applications.
Keywords: sol-gel process, tetrametoxysilane, hydrolysis, polycondensation, acidic environment.

Introduction

The term “sol-gel synthesis” covers a broad group of liquid-phase synthesis techniques characterized by the transition from sol to gel, typically yielding non-crystalline products with fractal-like structures. The overall process is controlled by temperature and, importantly, by catalytic conditions, particularly the acidic or basic environment in which the reactions occur. Due to its unique properties, the sol-gel method enables the fabrication of uniform, high-quality nanoparticles on an industrial scale [1]. Another significant advantage is the ability to obtain highly pure (up to 99.99%) and homogeneous composites [2].

During the sol-gel process, chemical precursors undergo hydrolysis and polycondensation, initially forming a nanodispersed sol [3]. The composition of the reaction medium, its pH, and the temperature determine the size of the particles and the degree of aggregation at this stage. In the final step, the construction of the gel network and the intensity of interparticle interactions define the mechanical and functional properties of the material [4]. The technique is commonly applied in the synthesis of metal oxides. These advantages make the sol-gel method a powerful route for producing materials with unique properties that are otherwise difficult or impossible to achieve by conventional techniques [5].

Despite its advantages, the sol-gel process also presents certain limitations. Precursors are highly sensitive to moisture, which restricts large-scale production–particularly in the field of optical coatings [6, 7]. Additionally, the process is time-consuming, since stabilization and careful drying steps are required to obtain monoliths or bulk materials (with the exception of thin coatings). Other technological challenges include substantial shrinkage of the gel and crack formation during drying.

The sol-gel process typically takes place at relatively low temperatures (usually below 100°C) in a

liquid medium, yielding a solid material [8]. These solids are formed through polymerization reactions involving the creation of M–OH–M or M–O–M linkages (where M denotes a metal atom). Several parameters influence the hydrolysis and condensation reactions, including precursor reactivity, the water-to-alkoxide ratio, pH of the medium, temperature, solvent nature, and the presence of additives [9]. Catalysts are frequently employed to regulate the rate and extent of hydrolysis and condensation. By adjusting these processing conditions, materials with diverse microstructures and surface chemistries can be obtained [10, 11].

The structural characteristics of materials derived from the sol-gel method can thus be easily tailored by varying synthesis parameters and conditions. The resulting materials typically exhibit nanoscale porosity, making them highly suitable for applications in catalysis, sensors, optoelectronic devices, and functional coatings. Their high surface area also enables use as chemical sorbents and catalyst support [12]. Furthermore, optically transparent layers and nonlinear optical materials prepared via this approach are of great significance for solar cells and optical fibers.

The versatility of the sol-gel technique has also been exploited in sensor fabrication, where porous and chemically modified surfaces enhance sensitivity and selectivity [13]. In addition, sol-gel chemistry enables the synthesis of bioactive glasses and ceramics, drug delivery systems, and implant coatings, whose importance in biomedical applications continues to grow. Other industrial applications include antibacterial coatings and corrosion-resistant layers. In the energy sector, the method is used for the preparation of high-performance components for supercapacitors, lithium-ion batteries, and solar panels, where porous structures with stable ion conductivity and tunable functionality are especially critical [14].

The objective of this study is to synthesize SiO_2-based nanoparticles under acidic conditions using the sol-gel method and to investigate the relationship between their structure and properties [15]. For this purpose, the effects of amides, solvent, and catalysts on the hydrolysis and polycondensation reactions of tetramethoxysilane were systematically studied [16].

Materials and methods

The synthesis of the silica matrix was carried out using the sol-gel method. This process enables the formation of inorganic networks under mild conditions and thus allows the stable incorporation of organic components.

In acidic medium, tetramethoxysilane (TMOS) was used as the main precursor. Since acid catalysis is essential for the hydrolysis and polycondensation of TMOS, hydrochloric acid was initially employed as the catalyst. The molar ratio of TMOS:water:ethanol was adjusted to 1:4:4. Owing to its strong acidity, HCl significantly accelerated the hydrolysis of TMOS, leading to the formation of silanol (Si–OH) groups. In practice, TMOS was first mixed with ethanol, followed by the addition of distilled water. The primary reaction at this stage proceeds as follows:

$$Si(OCH_3)_4+4H_2O\rightarrow Si(OH)_4+4CH_3OH \quad (1)$$

Subsequently, HCl was added as a catalyst, and the reaction mixture was stirred on an IKA C-MAG HS 7 magnetic stirrer with heating at 25-40°C for 2 h.

The silanol groups formed during hydrolysis underwent condensation reactions, producing a three-dimensional siloxane network:

$$Si(OH)_4+ Si(OH)_4\rightarrow HO–Si–O–Si–OH+H_2O \quad (2)$$

or

$$Si(OH)_4+Si(OCH_3)_4\rightarrow HO–Si–O– – Si– OCH_3+CH_3OH \quad (3)$$

To further improve the efficiency of the process and enhance the structural properties of the product, acetic acid (CH_3COOH) was used instead of HCl. The advantage of CH_3COOH lies in its ability to form volatile methyl esters (CH_3COOCH_3), which leave the reaction system, gradually changing the pH and thus optimizing the condensation stage. This leads to homogeneous, transparent, and crack-free monolithic gels:

$$CH_3COOH + CH_3OH\rightarrow CH_3COOCH_3+ H_2O \quad (4)$$

When CH_3COOH was employed as the catalyst, acetic acid was used as the solvent. To stabilize the system and improve gel formation, a series of amides were added:

1. Formamide [$H–C(NH_2)=O$]
2. Dimethylformamide [$H–C(N(CH_3)_2)=O$]
3. Diethylformamide [$H–C(N(C_2H_5)_2)=O$]
4. Diisopropylformamide [$H–C(N(i\text{-}C_3H_7)_2)=O$]
5. Acetamide [$CH_3–C(NH_2)=O$]
6. Dimethylacetamide [$CH_3–C(N(CH_3)_2)=O$]

These amides absorbed protons, gradually increasing the pH and creating favorable conditions for condensation. Upon protonation, they also formed ammonium salts as by-products:

$$R–CONH_2 + H^+ \rightarrow R–CONH_3^+ \quad (5)$$

After the addition of amides, the homogeneous sol was left to gel at room temperature for 8-12 h. The resulting gels were first dried at room temperature and subsequently subjected to gradual heating up to 50-90°C to ensure the complete removal of volatile by-products (water, methanol, and others), ultimately yielding crack-free monolithic gels.

To investigate the structure, phase composition, and morphology of the synthesized hybrid composites, scanning electron microscopy (SEM) was employed. These analyses provided information on the microstructural organization and structural integrity of the gels obtained under different synthesis conditions.

Results and discussion

The main stages of the sol-gel technology illustrate not only the general theoretical approach but also reflect the stepwise course of the synthesis processes carried out in the present study (Figure 1).

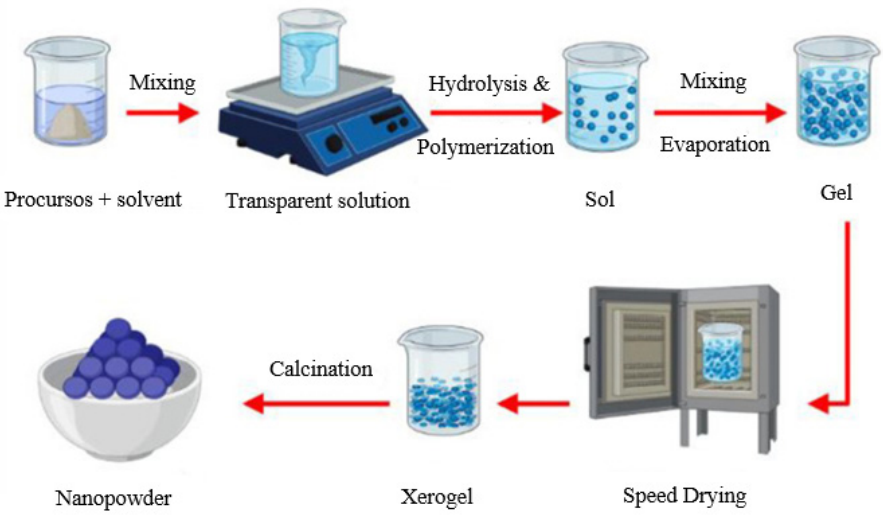


Figure 1 – Schematic representation of the main stages of the sol-gel process from precursors to gel [6]

The hydrolysis and polycondensation of the initial precursors first lead to the formation of a sol system, followed by the gradual transition of the structure into the gel phase. Consequently, the morphological and physicochemical properties of the obtained material are directly determined by the specific features of this mechanism.

Experimental observations demonstrated that the pH of the medium had a significant effect on the rates of hydrolysis and condensation during the sol-gel synthesis. At lower pH values, the hydrolysis reaction proceeded more rapidly, whereas condensation occurred relatively weakly. As the numerical value of pH increased, the rate of hydrolysis initially decreased gradually but began to increase again when the pH exceeded 7. At the same time, the rate of condensation decreased inversely with increasing pH.

Figure 2 illustrates the changes in the relative rates of hydrolysis and condensation reactions as a function of pH. Based on the obtained results, it was determined that the hydrolysis reaction proceeded rapidly at low pH values, but its rate gradually decreased as the pH approached 7. When the pH exceeded 7, a renewed increase in the hydrolysis rate was observed. In contrast, the condensation reaction was relatively weak under acidic conditions and became even weaker as the pH increased. According to the conducted experiments, pH = 4 and pH = 9.5 were evaluated as optimal media, where hydrolysis and condensation reactions occurred in a balanced manner.

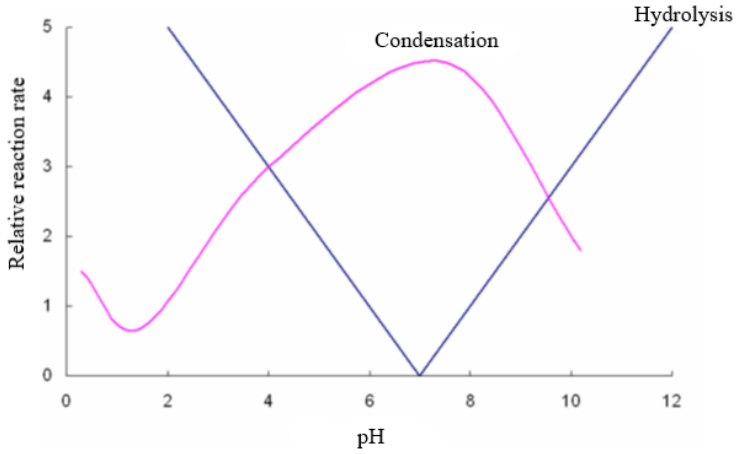


Figure 2 – Variation of the relative rates of hydrolysis and condensation reactions under different pH conditions

The acidity of the medium plays a crucial role in the sol-gel synthesis of monolithic (crack-free after drying) silica gels. Strongly acidic conditions (pH < 1) are optimal for hydrolysis, whereas near-neutral conditions (pH 4–5) favor condensation. Thus, the effect of pH variation on the physicochemical parameters of the resulting gels was investigated.

To modify the structure of sol-gel materials and obtain crack-free gel bodies, a series of organic amides (DCCA) were introduced into the system:

1. H-C(NH_2)=O (Formamide)
2. H-C(N(CH_3)$_2$)=O (Dimethylformamide)
3. H-C(N(C_2H_5)$_2$)=O (Diethylformamide)
4. H-C(N(i-C_3H_7)$_2$)=O (Diisopropylformamide)
5. CH_3-C(NH_2)=O (Acetamide)
6. CH_3-C(N(CH_3)$_2$)=O (Dimethylacetamide)

The DCCA-type additives (1–6), which regulate the drying process, facilitated the formation of larger and more uniformly sized pores within the gel network. In such pores, capillary forces are weaker, which reduces internal stress during drying and prevents crack formation in the material. Moreover, due to the higher vapor pressure in larger pores, solvent evaporation occurs more rapidly. In addition, the amides interact with hydrogen ions, and depending on their structure, these reactions proceed at different rates. The introduction of these compounds into the system enabled a gradual and controlled variation of acidity during the sol-gel process, with the rate of change differing according to the specific amide employed (Figure 3).

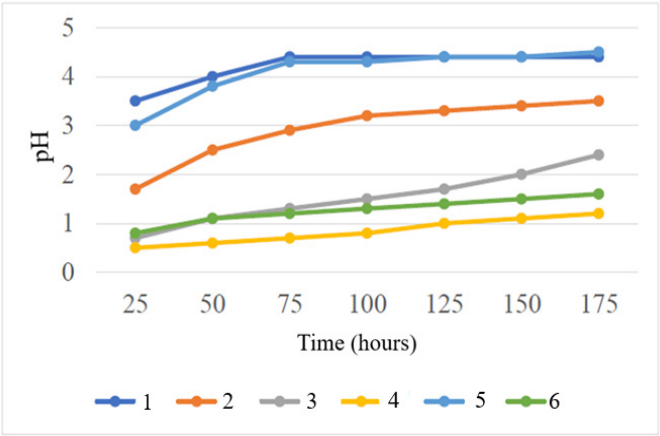


Figure 3 – Time-dependent pH variation in solutions of amides 1-6

Among all synthesized gels, only the samples obtained in the presence of amides 3/,4/,5/ were monolithic and transparent. The comparison of the physicochemical properties of the synthesized gels, including gelation time, density, and hardness, is presented in Table 1. It shows that gels prepared in the presence of diethylformamide (3) and dimethylacetamide (6) exhibited the highest density, mechanical strength, and the lowest microporosity. 7/ – gel obtained without any amide addition.

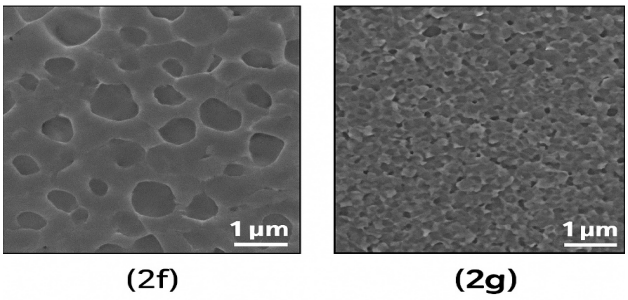
Physical-chemical characteristics of the obtained gels (Comparison of gelation times, density, and hardness of synthesized gels) are shown in table 1. Hydrolytic polycondensation of TMOS proceeds most effectively when the hydrolysis rate of the amides adapts to the medium's acidity. During gelation, an optimal gradual pH shift from 0.7–0.9 to 1.8–2.5 ensures efficient hydrolysis and polycondensation. Among the studied amides, diethylformamide (3) and dimethylacetamide (6) were found to be more effective as DCCA reagents (drying-controlling additives) compared to formamide (1) and dimethylformamide (2). Moreover, it was demonstrated that the commonly applied amounts of DCCA (1–3 equivalents per 1 mol of tetrametoxysilane) are excessive; the optimal dosage should not exceed 0.1–0.2 equivalents to achieve controlled gelation and uniform pore structure.

Table 1 – Physical-chemical characteristics of the obtained gels

Samples	Gelation time	SiO_2, %	Density, g/cm³	Hardness, kg/mm²
1/	2.23	2.23	2.23	-
2/	9.78	9.78	9.78	56
3/	8.40	8.40	8.40	70
4/	7.83	7.83	7.83	35
5/	12.03	12.03	12.03	-
6/	8.45	8.45	8.45	112
7/	6.58	6.58	6.58	54

According to the scanning electron microscopy (SEM) results of the synthesized gels, specifically samples 6/ and 7/ as shown in Figure 4, significant differences in the microstructural organization can be observed.

The gel sample 6/, which was prepared by introducing dimethylacetamide (1) into the reaction system, exhibits a markedly more ordered and homogeneous network compared to gel 7/, which was synthesized without the addition of any amide. The reason why 6/ has greater structural unity and less porosity can be found in the molecular control exercised by dimethylacetamide in the sol-gel transition. Thus, dimethylacetamide acts as a molecular control agent that affects the silanol groups in the sol-gel transition. Since the presence of silanol groups triggers the hydrolysis step in a sol-gel transition, dimethylacetamide slows down the rate of the sol-gel transition. Therefore, there is more careful nucleation of a silica framework in 6/. Hence, the result is a more evenly distributed silica framework with fewer defects in 6/. Consequently, 6/ becomes more denser on the inside; therefore, the structural integrity of 6/ increases.



Sample 6/ Sample 7/

Figure 4 – SEM images of samples obtained with dimethylacetamide and without any amide

In addition, a more compact micromorphology of the gel would be expected to positively affect the performance results when uniformness of structure, mechanical strength, and non-porosity are desired, as in optical films, supports of catalysts, or carrier matrices for biomedical purposes. In this way, the tests carried out above show the primary effect of amide additives on the control and development of morphology and functionality of sol-gel-based SiO_2 polymer composites.

Conclusion

This work includes an examination of sol–gel processing of silicon dioxide-based materials synthesized with an acidic medium with attention to both kinetics of hydrolytic polycondensation of tetrametoxysilane and application of amide-based additives for drying control.

The results showed that the acidity of the reaction environment exerts a great influence on the hydrolysis of silicon-alkoxy groups and their further

condensation into silicon-oxygen-silicon (Si-O-Si) bonds that control the properties of the gel network, transparency, and mechanical properties. Weakly acidic media favor slower gelation processes with the formation of porous gels of low mechanical strength in contrast to the use of strong acids, especially acetic, which provide a more homogeneous, transparent, and rigid gel with a well-distributed pore structure. Moreover, the work has shown that the influence of amide additive composition and content exerts a great influence on the gelation processes. The best agents regulating drying are diethylformamide and dimethyl-acetamide used in comparison with other amides.

The application of common higher concentrations proved unnecessary, whereas a lower quantity corresponding to 0.1–0.2 of reactive species was adequate for the controlled gelation and formation of nanostructure. The results offer a sound scientific basis for the preparation of silica-based gels with specific structural features and properties. Based on the control over acidity in the medium along with the addition of proper amide agents, monolithic gels with improved mechanical properties can be prepared. Overall, this work enhances the understanding of reaction kinetics and mechanisms in sol–gel processes and offers practical guidance for developing highly functional hybrid materials applicable in optical, catalytic, and biomedical technologies.

Conflict of interest

The authors declare that they have no conflicts of interest.

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