

PREPARATION OF ORGANIC-INORGANIC COMPOSITE MATERIALS USING SOL-GEL TECHNOLOGY

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ABSTRACT

This article reviews the principles of hydrolytic polycondensation of tetramethoxysilane (TMOS) in alkaline media. Depending on the concentration of tetramethoxysilane, both nanoscale monodisperse SiO₂ particles and monolithic samples of xerogels were synthesized. Pyridine derivatives, representatives of several chemically and thermally stable aromatics, which perform the function of catalysts, were selected for the work. During the sol-gel process of hydrolysis of tetramethoxysilane and the polycondensation of the compounds formed with the presence of 4-(dimethylamino)-pyridine as a catalyst, a linear increase in the pK_a of the conjugate acid to 9.70 was observed. Since the particles formed in an alkaline environment are negatively charged and repel each other, their growth occurs by the condensation mechanism due to the dissolution of smaller particles.

Heating the sol-gel system for 30 minutes does not increase the particle size, but brings the gelation point closer. Thus, a small amount of catalyst leads to the formation of a group of particles with a small diameter and a tendency to polycondensate, but a larger amount of catalyst concentration causing the formation of very large particles. The physico-chemical properties of the synthesized particles were determined. The dimensions of the processed samples were recorded using a scanning electron microscope (SEM).

Keywords: Sol-gel, hydrolysis, polycondensation, tetramethoxysilane, xerogel, pK_a, catalyst, SEM.

Introduction

The history of sol-gel technology has been reviewed based on functional materials derived from sol-gel. Around the 1970s, significant sol-gel processing began worldwide efforts and was recognized as a new method for preparing homogeneous glasses and ceramics at low temperatures. However, after the preparation of inorganic-organic hybrid materials by the sol-gel method was proposed in 1984, glass and ceramic researchers used the sol-gel method to develop functional materials with optical, electrical, chemical, and mechanical functions, as well as advanced glasses and ceramics. they started processing. Around 1995, sol-gel technology attracted people working in all areas of materials technology, including electronics, chemistry, mechanics, pharmaceuticals, and medicine.

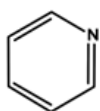
The sol-gel process is widely used to develop efficient and advanced materials, including silica-based xerogels, which can be tailored for specific environmental applications.

Thus, the aim of the research is to synthesize monolithic samples of nano-sized monodisperse

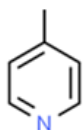
SiO₂ particles and xerogels depending on the density of tetramethoxysilane using the sol-gel method and to determine their physico-chemical parameters.

Material and methods

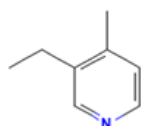
Using the sol-gel method, nanoscale monodisperse SiO₂ particles and monolithic samples of xerogels are synthesized. The obtained samples are based on the principles of hydrolytic polycondensation of tetramethoxysilane (TMOS) in an alkaline medium. Thus, chemically and thermally stable pyridine derivatives were selected for work:



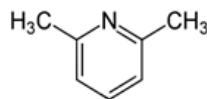
(1) Pyridine



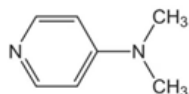
(2) 4-methyl pyridine



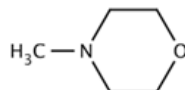
(3) 3-ethyl-4-methyl pyridine



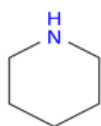
(4) 2,6-dimethyl pyridine



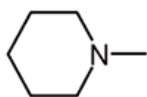
(5) 4-dimethyl amino pyridine



(6) n-methyl morpholine

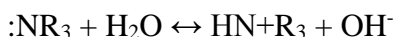


(7) Piperidine



(8) n-methyl piperidine

Organic amines are used as catalysts, and their choice is determined by the pK_a of conjugated acids of organic amines.



The best way to measure the basicity of an amine is to examine the pK_a of its conjugate acid. The higher the pK_a of the conjugate acid, the stronger the base. So, to calculate the pK_a value of the combined acid (HN⁺R₃) according to the above reaction, the ionization constant (K_a) of the acid was calculated:

First, based on the following formulas K_a, and then the numerical value of pK_a was calculated:

$$K_a = \frac{[HN^+R_3][OH^-]}{[NR_3]}, \quad pK_a = -\log K_a = -\log \left\{ \frac{[HN^+R_3][OH^-]}{[NR_3]} \right\}$$

In the sol-gel process, a monolithic SiO₂ xerogel is synthesized in an alkaline environment when a certain amount of solvent (ethanol, 1 equivalent) and water (4 equivalent) is used for 1

mol of TMOS. The following amines are used in the work:

- (1a) Pyridine
- (1b) 2-fluoropyridine
- (1c) Methyl pyridine
- (1d) N-methyl morpholine
- (1e) N-methyl piperidine
- (1f) 1-Ethyl-2,2,6,6-tetra methyl piperidine

A scanning electron microscope (SEM) is used to obtain accurate images of the synthesized particles. An SEM is a type of electron microscope that uses electrons instead of light to create a magnified, clear image. Particles were examined using a Scanning Electron Microscope with a Secondary Electron Detector (SE).

Results and discussion

Based on the conducted research, monolithic samples of nano-sized monodisperse SiO₂ particles and xerogels were synthesized as a result of hydrolytic polycondensation of tetramethoxysilane (TMOS) in an alkaline medium. During the sol-gel process of TMOS hydrolysis, a linear increase in the pKa value of 9.70 was observed in the polycondensation of compounds formed with the presence of 4-(dimethylamino)-pyridine as a catalyst.

Images of synthesized particles were obtained by scanning electron microscope (SEM). According to the observations, the particle size at 0,35 mol·l⁻¹ of amine concentration was 10 nm, and at 7 equivalent concentrations, the particle size was recorded as 210-240 nm. Small diameter particles were formed as a result of the fact that the small amount of the used catalyst does not ensure high breaking and formation of Si-O-Si bonds. However, due to the high concentration of spent catalyst, larger diameter particles were synthesized.

Taking 4-methyl pyridine(2) (pKa 6.02) as catalyst required at least 4 h at 70°C to obtain SiO₂ particles, which hardly appeared in the sol-gel process. In the presence of 3-ethyl-4-methyl pyridine(3) (pKa 6.46) catalyst, the SiO₂ particles formed during the same period had a slightly larger diameter. When the amino-pyridine (1) with the least basicity was used for the work process, it was kept in the sol-gel system at 70°C for 8 hours, and then for an additional 8 days at room temperature. Only then were the particles discovered. Such behavior of sol-gel systems (1-3) is explained by the increase in the basicity of amines used in them. However, heating of the sol-gel system with 2,6 dimethylpyridine (4) (pKa 6.77) as catalyst for 4 hours did not reveal particles, although the base of this compound is pyridine, 4-methyl pyridine and 3-ethyl-4-methyl significantly higher than pyridine amines. Thus, the mechanism of formation of SiO₂ nanoparticles in the presence of organic amine is based on the ability of a free electron pair of a nitrogen atom to attack a silicon atom. When this pair of electrons is less accessible, the sol-gel process becomes more difficult due to the hindrance created by the two methyl groups. That is, in this case, the occurrence of the sol-gel process is determined by the nucleophilicity of the catalyst, not by basicity.

The diameter of the SiO₂ particles obtained in the presence of N-methylmorpholine (6) was 10 nm. As the amine basicity increases, the particle size of SiO₂ increases in the order N-methylmorpholine (6) < 4-(dimethylamino)pyridine (5) N-methylpiperidine (8) << piperidine (7).

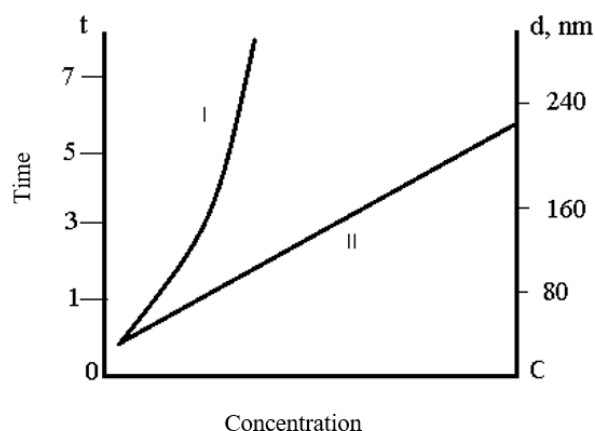


Fig. 1. Plot of the formation time and mean particle sizes of the particles formed in the sol-gel system as a function of concentration

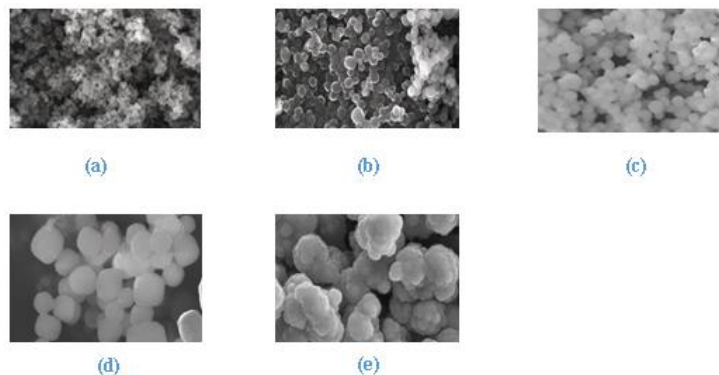


Fig. 1. Scanning Electron Microscope (SEM) images of particles in sol-gel systems, 100000x magnification

Physico-chemical properties of synthesized xerogels are listed in table 1.

Table 1. Physico-chemical characteristics of the obtained samples

Sol-gel system	t, hour	SiO ₂	C	pK _a	Density gr·cm ⁻³	Hardness	Yield percentage of the purchased product, %
		%					
2a	0.77	88	2.05	3.0	1.07	32.6	46.8
2b	0.18	89.5	3.35	5.25	0.73	11.1	63.2
2c	0.13	90	4.55	6.0	0.66	15.7	66.7
2d	0.02	92	1.75	7.41	-	9.4	-
2e	< 0.01	91	1.45	9.97	0.58	9.2	71.3
2 f	< 0.01	91	2.70	11.13	0.65	15.4	67.9
2 h	< 0.01	94	1.0	9.25	-	10.0	-

From the above data, it is clear that as the basicity of amines used as a catalyst increases, their density and hardness decrease with the increase of porosity of the synthesized samples. At this time, the percentage amount of gel SiO₂ increases, and at the same time, the gelation time (t)

of the sol-gel system decreases.

Conclusions

Hydrolytic polycondensation of tetramethoxysilane (TMOS) in alkaline medium was carried out, as a result of which both nanoscale monodisperse SiO₂ particles and monolithic samples of xerogels were synthesized, depending on the density of TMOS.

At a concentration of 0,35 mol·l⁻¹ of amines taken as a catalyst, the particle size limit was determined 10 nm, and at a concentration of 7 equivalents, the size of the formed particles was 210-240 nm.

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ÜZVİ VƏ QEYRİ- ÜZVİ KOMPOZİT MATERİALLARININ SOL-GEL TEKNOLOGİYASI İSTİFADƏSİ İLƏ HAZIRLANMASI

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XÜLASƏ

Bu məqalə qələvi mühitdə tetrametoksisilanın (TMOS) hidrolitik polikondensasiyası prinsiplərini nəzərdən keçirir. Tetrametoksisilanın konsentrasiyasından asılı olaraq həm nanoölçülü monodispers SiO₂ hissəcikləri, həm də kserogellərin monolit nümunələri sintez edilmişdir. İş üçün

katalizator funksiyasını yerinə yetirən bir neçə kimyəvi və termal stabil aromatlərin nümayəndələri olan piridin törəmələri seçilmişdir. Tetrametoksisilanın hidrolizinin sol-gel prosesində və katalizator kimi 4-(dimetilamino)-piridin iştirakı ilə əmələ gələn birləşmələrin polikondensasiyası zamanı konyuq turşunun pKa-nın 9,70-ə qədər xətti artım müşahidə edilmişdir. Qələvi mühitdə əmələ gələn hissəciklər mənfi yüklü olduğundan və bir-birini itələdiklərindən, onların böyüməsi daha kiçik hissəciklərin həll olması hesabına kondensasiya mexanizmi ilə baş verir.

Sol-gel sisteminin 30 dəqiqə qızdırılması hissəciklərin ölçüsünü artırmır, lakin gəlləşmə nöqtəsini yaxınlaşdırır. Beləliklə, az miqdarda katalizator kiçik diametrlə və polikondensata meyilli hissəciklər qrupunun meydana gəlməsinə səbəb olur, lakin daha çox miqdarda katalizator çox böyük hissəciklərin meydana gəlməsinə səbəb olur. Sintez edilmiş hissəciklərin fiziki-kimyəvi xassələri müəyyən edilmişdir. İşlənmiş nümunələrin ölçüləri skan edən elektron mikroskopu (SEM) istifadə edərək qeyd edildi.

Açar sözlər: Sol-gel, hidroliz, polikondensasiya, tetrametoksisilan, kserogel, pKa, katalizator, SEM.

ПОЛУЧЕНИЕ ОРГАНИЧЕСКО-НЕОРГАНИЧЕСКИХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ ПО ЗОЛЬ-ГЕЛЬ-ТЕХНОЛОГИИ

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РЕЗЮМЕ

В статье рассмотрены принципы гидролитической поликонденсации тетраметоксисилана (ТМОС) в щелочных средах. В зависимости от концентрации тетраметоксисилана были синтезированы как наноразмерные монодисперсные частицы SiO₂, так и монолитные образцы ксерогелей. Для работы были выбраны производные пиридина – представители нескольких химически и термически стабильных ароматических соединений, выполняющих функцию катализаторов. В ходе золь-гель процесса гидролиза тетраметоксисилана и поликонденсации образующихся соединений в присутствии 4-(диметиламино)пиридина в качестве катализатора наблюдалось линейное увеличение pKa сопряженной кислоты до 9,70. Поскольку частицы, образовавшиеся в щелочной среде, заряжены отрицательно и отталкиваются друг от друга, их рост происходит по конденсационному механизму за счет растворения более мелких частиц.

Нагревание золь-гель системы в течение 30 минут не приводит к увеличению размера частиц, но приближает точку гелеобразования. Так, небольшое количество катализатора приводит к образованию группы частиц малого диаметра и склонности к поликонденсации, а большее количество катализатора вызывает образование очень крупных частиц. Определены физико-химические свойства синтезированных частиц. Размеры обработанных образцов фиксировались с помощью сканирующего электронного микроскопа (СЭМ).

Ключевые слова: золь-гель, гидролиз, поликонденсация, тетраметоксисилан, ксерогель, pKa, катализатор, СЭМ.