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Effect of silicic acid concentration on green mesoporous silica synthesis

Efecto de la concentración del ácido silícico en la síntesis de sílices

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Abstract

Tetraethoxysilane is the most commonly used precursor for obtaining mesoporous silica, it is economically expensive, so the use of inexpensive precursors such as sodium silicate or silicic acid are of interest for the economic production of said materials; silicic acid is generally obtained from sodium silicate by adjusting the pH of the system to 3-4 or through the use of ion exchange resins, this second methodology allows to eliminate the use of acid or basic catalysts in the synthesis of materials, which potentiates these materials for bioparticle encapsulation applications. The effect of the poly-condensation of silicic acid in obtaining mesoporous silica has been little evaluated, so this work shows the study of the effect of the degree of polycondensation of silicic acid on the textural properties of the materials, observing that at 0 and After 48 h of $Si(OH)_4$ aging, the synthesized materials show a bimodal distribution of their pores at 4 and 8 nm, observing the majority presence of pores at 4 nm at 6, 24 and 72 h of aging.

Mesoporous silica, Silicic acid precursor, Effect

Resumen

El tetraetóxisilano, es el precursor más comúnmente utilizado para la obtención de sílice mesoporosa, este es económicamente costoso, por lo que el uso de precursores económicos como el silicato de sodio o el ácido silícico son de interés para la obtención económica de dichos materiales; el ácido silícico se obtiene generalmente a partir de silicato de sodio a partir del ajuste del pH del sistema a 3-4 o mediante el uso de resinas de intercambio iónico, esta segunda metodología permite eliminar el uso de catalizadores ácidos o básicos en la síntesis de los materiales, lo cual potencializa estos materiales para aplicaciones de encapsulación de biopartículas. El efecto de la policondensación del ácido silícico en la obtención de sílices mesoporosas ha sido poco evaluado, por lo que el presente trabajo muestra el estudio del efecto del grado de policondensación del ácido silícico en las propiedades texturales de los materiales, observándose que a 0 y 48 h de añejamiento del $Si(OH)_4$, los materiales sintetizados muestran una distribución bimodal de sus poros a 4 y 8 nm, observándose la presencia mayoritaria de poros a 4 nm a 6, 24 y 72 h de añejamiento.

Sílice mesoporosa, Acido silícico precursor, Efecto

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Introduction

Mesoporous and functionalized mesoporous silica material has been an important application and interest in the material science, for example, has been widely used in the removal of contaminants (ion metallic and no metallic, dyes and different organic compound), as support catalytic, optic application, and diverse biologic application (control release drug system, support of biomolecule) [1-6]. Usually, the TEOS (tetraethoxysilane) is used as a precursor of silica matrix in the synthesis of these materials, this precursor has the disadvantage of being very expensive, so the use of other silica precursors is more economic as the sodium metasilicate (Na_2SiO_3) has been proposed in these materials syntheses [7-13].

The bioinspired synthesis route from sodium metasilicate and different polyamines as condensation catalysis and tailored material allow the obtained hollow silica mesoporous and another green silica [7-9], which has been used in the removal of formaldehyde and Hydrocarbons from the air [8,9, 12], in the adsorption of pesticide [ref] and biomolecule [10-13]. The capacity of adsorption of these green silica materials has been reported as similar to the adsorption capacity of conventional mesoporous silica obtained from TEOS. These reports show the possible use of more economic precursors in the syntheses of mesoporous silica materials

In these route syntheses, the Si $(OH)_4$ is the silica precursor material and is produced by the acid-adjusted pH in the silicate solution or by ion exchange resin [7-18]. The silica obtained from ion exchange resin allows the best biomolecule (enzyme) encapsulation and offers biomolecule protection because in the material syntheses could be not used acid or base catalyst, avoiding the denaturation of the biomolecule and best activity biologic.

This paper shows the effect of silicic acid concentration initial in the textural properties of green silica mesoporous obtained.

Experimental Section

Si $(OH)_4$ Obtained

Si $(OH)_4$ was obtained from sodium silicate industrial grade. 100mL of sodium silicate 25% previously filtered was passed through of exchange ion resin (Dowex 50WX8 hydrogen form) and the Si $(OH)_4$ was eluted with deionized water, was recollected the portion at pH 1-4 and aged by 0, 6, 12, 24, 48 and 72 h from evaluated the effect of the concentration of Si $(OH)_4$ in the textural properties of mesoporous silica obtained.

The Si $(OH)_4$ concentration, was determined from yellow silicic- molybdenum complexes by Uv-visible determination at λ 400nm [14-15]

Synthesis of Mesoporous Silica (MS)

The mesoporous silica (MS) was obtained by hydrothermal process. The silicic acid was a mixture with a solution Pluronic, P-123 (66 g with 500mL H_2O) at ration 1:2, the mixture was collocated at 50-60°C for 24 h and the solid obtained was recovery from filtration. The Pluronic was eliminated by calcination from 4 h at 600°C.

The textual properties was evaluated by adsorption-desorption of N_2 isotherms at 77 K in a Micromeritics ASAP-2010 instrument. The samples were degassed overnight at 180 °C and 7l mmHg before measurements; the surface area was calculated using the BET method, and the average pore diameter was calculated applying the BJH method to the desorption branch of the isotherm.

Result

The effect of acid silicic initial concentration in the textural properties of green mesoporous silica synthesis (MS) is resume in the Table 1. The silicic acid was aged at 0, 6, 24, 48, and 72 h. The initial solution of Si $(OH)_4$ obtained from exchange ion show an initial concentration of 626 mgL^{-1} of $Si(OH)_4$, determined by the Deutschen- Einheitsverfahren method (molybdenum-silicic complex).

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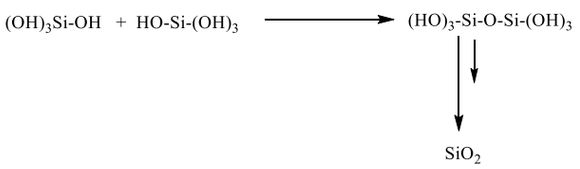
The aged of this solution allows obtained mesoporous materials with isotherm type IV (Figure 1) and with different modal pore distribution; the materials obtained at 0 h aged show a bimodal distribution with pores at 3.9 and 10.86 nm, however, the aged of Si $(OH)_4$ on Pluronic solution produce materials with one pore at 3.9 nm.

The 72 h of aged showed again the bimodal distribution at 3.9 and 7 nm pore, this behavior, suggests that each 48 h of aged the bimodal pore distribution at 4 and 7 nm could be obtained (Figure 2). The aged of silicic acid produced the polymerization of this according at scheme 1 and the formation of different oligomer that allow the condensation of pore at 10 nm closed at 3 nm of diameter. The proportion of oligomer of lager size at more time of aged show the formation of bimodal mater with pore at 4 and 7 nm. All materials obtained show superficial area at 444-624 m^2g^{-1} similar at reported from silica materials synthesis from Si $(OH)_4$ or silicate. The use of other molecular sieves of different sizes could allow the design of size pore and the aged solution the modal distribution.

The kinetic of condensation of Si $(OH)_4$ is show in the Figure 3, was observed an adjusted of experimental date at the second order kinetic model, observed an constant of $4X10^{-4}$ $Lmg^{-1}h^{-1}$. According to kinetic studies the condensation process is show in the scheme 1.



Scheme 1 Poly-condensation of silicic acid

	MS-0h	MS-6h	MS-24h	MS-48h	MS-72h
Aged time[h]	0	6	24	48	72
$[Si(OH)_4]_0$ (mgL^{-1})	626.1	265.9	97.7	52.9	36.3
A_{BET} [m^2g^{-1}]	444.5	496.5	491.4	465.6	624.2
Diameter Pore Average [nm]	4.99	3.62	3.90	4.87	3.71
Volume Pore Average [cm^3g^{-1}]	0.55	0.41	0.34	0.49	0.48
Diameter Pore (BJH) [nm]	3.9 and 10.9	3.9	3.9	3.9	3.9 and 7.8
External Surface Area [m^2g^{-1}]	352.8	386.0	336.6	361.4	438.7

Table 1 Textural properties of Mesoporous Silica obtained at the different aged times

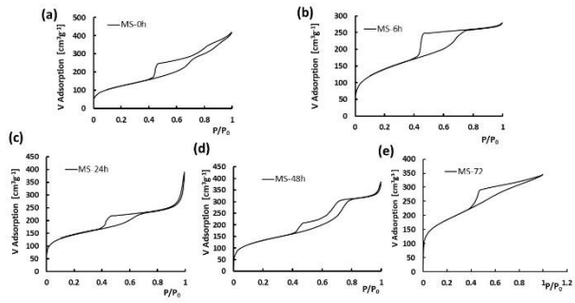


Figure 1 Isotherm adsorption-desorption of MS at 0 h (a), 6 h (b), 24 h (c), 48 h (d) and 72 h (e) aged.

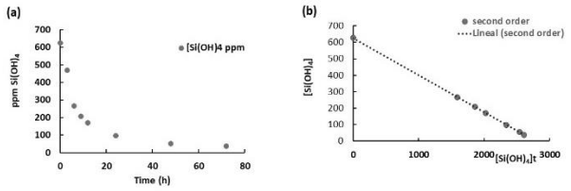


Figure 2 BJH pore distribution of MS at 0 h (a), 6 h (b), 24 h (c), 48 h (d) and 72 h (e) aged.

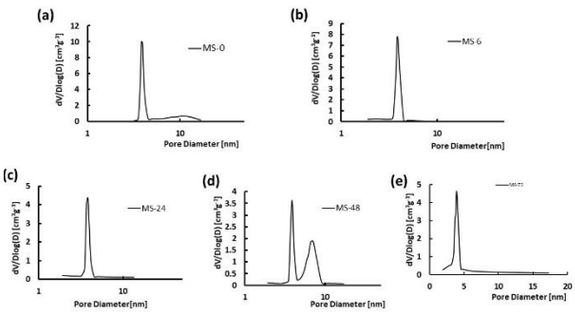


Figure 3 Kinetic studies of silicic acid condensation

Conclusion

The aged of acid silicic, allow the formation of oligomer of different size that could generated materials mono o bimodal. The bimodal materials was observed with 0 and 72 h of aged. The use of other molecular sieves of different sizes could allow the design of size pore and the aged solution the modal distribution.

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References

[1] Mahdieh Darroudi, Ghodsi Mohammadi Ziarani, Jahan B.Ghasemi, Shahriyar Bahar, Alireza Badiei "SBA-ionic liquid as an efcient adsorbent of palladium, silver, and gold ions" *Journal of the Iranian Chemical Society* **(2022)** 19:247–255. https://doi.org/10.1007/s13738-021-02302-z

[2] Jal P K, Patel S, Mishra B K "Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metals ions" *Talanta*, **(2004)** 62: 1005-1028. https://doi.org/10.1016/j.talanta.2003.10.028

[3] Soltani, R., Pelalak, R., Pishnamazi, Marjani A., Albadrin A. B., Sarkar S. M., Shirazian S. "Synthesis of multi-organo-functionalized fibrous silica KCC-1 for highly efficient adsorption of acid fuchsine and acid orange II from aqueous solution". Sci Rep, (2021), 11:2716. https://doi.org/10.1038/s41598-021-81080-3

[4] J. Dobrzyńska, M. Dąbrowska, R. Olchowski, E. Zięba, R. Dobrowolski, "Development of a method for removal of platinum from hospital wastewater by novel ion-imprinted mesoporous organosilica" *Journal of Environmental Chemical Engineering* **(2021)** 9(4): 105302. https://doi.org/10.1016/j.jece.2021.105302.

[5] Shahid M., Bashir S., Habib A., Jamil A., Afzal A., Iqbal N. "Fabrication of Silica-Supported Al-Doped ZnO and Its Use in the Elimination of the Toxic Organic Ingredients from Industrial Effluents" ChemistrySelect (2021) 6(39): 10501-10513. https://doi.org/10.1002/slct.202102291.

[6] Paris, J. L., Colilla M., Izquierdo I., Manzano M., Vallet-Regí M. "Tuning mesoporous silica dissolution in physiological environments: a review." Journal of Materials Science 52 (2017): 8761-8771. DOI:10.1007/s10853-017-0787-1

[7] Method Joseph R.H. Manning, Eleni Routoula, Siddharth V. Patwardhan. Preparation of Functional Silica Using a Bioinspired J. Vis. Exp. (2018), e57730, DOI:10.3791/57730

[8] Abdunaser M. Ewlad-Ahmed, Michael Morris, Justin Holmes, David J. Belton, Siddharth V. Patwardhan, Lorraine T. Gibson. Green Nanosilicas for Monoaromatic Hydrocarbons Removal from Air. Silicon (2021). https://doi.org/10.1007/s12633-020-00924-1Abdunaser M. Ewlad-Ahmed, Michael A. Morris, Siddharth V. Patwardhan, Lorraine T. Gibson. Removal of Formaldehyde from Air Using Functionalized Silica Supports. Environ. Sci. Technol. (2012) 46: 13354−13360. https://doi.org/10.1021/es303886q

[10] David J. Belton, Siddharth V. Patwardhan, Vadim V. Annenkov, Elena N. Danilovtseva, Carole C. Perry. From biosilicification to tailored materials: Optimizing hydrophobic domains and resistance to protonation of polyamines. PNAS (2008) 105(16): 5963–5968. https://www.pnas.org/doi/10.1073/pnas.0710809105

[11] Shanyu Zhao, WimJ. Malfait, Eunho Jeong, Beatrice Fisher, Yucheng Zhang, Haixun Xu, Emanuele Angelica, William M. Risen Jr., J. William Suggs, Matthias M. Koebel. Facile one pot synthesis of mechanically robust biopolymer silica nanocomposite aerogel by cogelation of silicic acid with chitosan in aqueous media. ACS Sustainable Chem. Eng. (2016) 4: 5674-5683. https://doi.org/10.1021/acssuschemeng.6b01574

[12] Dong Wang, Jian Wang, Yuan Hu. Low cost synthesis of hollow mesoporous silica spheres and its application in the removal of aromatic volatiles. Materials Letters (2017) 208: 50-53. https://doi.org/10.1016/j.matlet.2017.05.016

[13] Alan R. Bassindale, Peter G. Taylor, Vicenzo Abbate, Kurt F. Brandstadt. Simple and mild preparation of silica-enzyme composite from silicic acid solution. J. Mater. Chem. (2009) 19: 7606-7609. https://doi.org/10.1039/B916412J

ISSN: 2410-3454

[14] Peggy Rimmelin-Maury, Thierry Moutin, Bernard Quéguiner. A new method for nanomolar determination of silicic acid in seawater. Analytica Chimica Acta (2007) 587: 281–286. doi:10.1016/j.aca.2007.01.055

[15] Julien Floch, Stéphane Blain, Dominique Birot, Paul Treguer. In situ determination of silicic acid in sea water based on FIA and colorimetric dual-wavelength measurements. Analytica Chimica Acta (1998) 377(2-3): 157-166. https://doi.org/10.1016/S0003-2670(98)00326-2

[16] Abdul Razak, Nurina Adriana, Nur Hidayati Othman, Muhammad Shafiq Mat Shayuti, Aidah Jumahat, Napisah Sapiai and Woei Jye Lau. "Agricultural and industrial waste-derived mesoporous silica nanoparticles: A review on chemical synthesis route." *Journal of Environmental Chemical Engineering* (2022), 10(2): 107322. https://doi.org/10.1016/j.jece.2022.107322.

[17] Sampedro-Guerrero, Jimmy Andrés, Vicente Vives-Peris, Aurelio Gómez-Cadenas and Carolina Clausell-Terol. "Improvement of salicylic acid biological effect through its encapsulation with silica or chitosan." *International Journal of biological macromolecules* (2022), 199: 108-120. https://doi.org/10.1016/j.ijbiomac.2021.12.124.

[18] Pratibha Sharma, Jai Prakash, Raj Kaushal, "An insight into the green synthesis of SiO_2 nanostructures as a novel adsorbent for removal of toxic water pollutants" Environmental Research (2022) 212 (Part. C): 113328. https://doi.org/10.1016/j.envres.2022.113328.

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