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Obtaining and Characterization of Porous Microspheres of Nb_2O_5, TiO_2 and their Mixtures by Internal Gelation

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The utilization of niobium oxide and its compounds has seen significant growth in recent years, with applications in ion exchangers, adsorbents, catalysts, supports, photocatalysts, and components of lithium and sodium batteries and capacitors. Brazil, having the world's largest niobium reserves, aims to lead in related technologies. This study synthesized mesoporous Nb_2O_5 microspheres via emulsification/internal gelation from reactive $NbCl_5$, developing a method to stabilize niobium pentachloride in aqueous solution. The microspheres were characterized for morphology, structural integrity (SEM), crystalline structure (XRD), and specific surface area and porosity (gas adsorption, N_2). Additionally, TiO_2 microspheres (from $TiCl_4$) and their mixtures with Nb_2O_5 in mol ratios 81/19 and 93/7 were obtained and characterized. The stabilization of $NbCl_5$ in aqueous solution was efficient, enabling the synthesis of Nb_2O_5 microspheres and their TiO_2 mixtures.

Keywords: *Microspheres, Nb_2O_5, internal gelation, TiO_2, photocatalysis.*

1. Introduction

Niobium is regarded as a strategic element due to the numerous properties and applications of its compounds, whether as metals, salts, oxides, or others. Over the past three decades, there has been a growing interest in developing new technological applications for Nb compounds-based materials across various fields. This underscores the critical importance of research and innovation in this area, particularly in Brazil, which not only holds the largest natural reserves of niobium in the world but is also the leading producer of its compounds[1-6].

Among the various applications, one that has been extensively explored is the use of niobium-based oxides in photocatalysis, proving to be a promising alternative to titanium oxide, the more commonly studied photocatalyst, or a possible mixing compound to improve efficiency. Niobium oxide (Nb_2O_5) has several interesting properties that allow it to be used in a wide range of applications. These properties include chemical stability and corrosion resistance in acidic and basic environments, low citotoxicity and chemical inertness, insolubility in water, and high photocatalytic activity with a band gap energy of 3.4 eV, which is quite similar to that of TiO_2[2,7,8].

Titanium oxide (TiO_2) is a semiconductor with a band gap of 3.2 eV that can be excited by UV light. It is chemically stable and corrosion resistant, and can generate highly reactive free radicals, enabling the degradation of organic pollutants and the purification of air and water through photocatalysis. In addition to its use as a photocatalyst, TiO_2 is currently utilized in solar cells, pigments for painting, and plastics[9].

The combination of TiO_2 and Nb_2O_5 in composite materials offers several notable advantages, as highlighted in the literature. This mixture enhances photocatalytic properties due to the synergy between the oxides. Titanium oxide, particularly in the anatase phase, is renowned for its superior performance as a photocatalyst, especially in processes excited by UV light, due to its band gap energy. Nb_2O_5, in turn, contributes to increasing chemical stability and corrosion resistance, in addition to improving charge separation efficiency and reducing electron-hole recombination. The synergy between these two oxides gives rise to a material with enhanced properties, making it a promising candidate for various technological applications, including photocatalysis, removal of pollutants, and the development of advanced electronic devices and biomaterials. This composite material exhibits the optimal characteristics of both oxides, thereby ensuring superior performance across a range of technological applications[10].

The internal gelation process was initially developed to produce U_2O_3 microspheres, which were subsequently utilized as nuclear fuel for HTGR (High Temperature Gas-Cooled Reactor) reactors. In summary, the process involves the cold mixing (below 5 °C) of a solution containing metal ions of interest with another solution containing organic compounds that act as gelling agents. The mixture is then dropped into a heated immiscible medium (between 70 and 95 °C), which promotes chemical reactions of hydrolysis and condensation that lead to the gelation of the droplets into a spherical shape. The advantages of this method include structural stability, compositional uniformity, size control, and reduction of defects[11].

In this study, microspheres of niobium oxide, titanium oxide, and their mixtures were synthesized using the emulsification/internal gelation technique, an adaptation of the traditional internal gelation process. After washing,

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drying, and calcination, the microspheres were subjected to a series of characterizations to assess their morphology and integrity using scanning electron microscopy (SEM). The crystalline structure was analyzed by X-ray diffraction (XRD), while the specific surface area and porosity were determined by nitrogen (N_2) adsorption using the BET and BJH models.

2. Materials and Methods

The reagents employed in the synthesis of microspheres by means of the internal gelation process included hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, P.A., Casa Americana), urea ($(NH_2)_2CO$, P.A., Casa Americana), niobium pentachloride ($NbCl_5$, CBMM), hydrogen peroxide (aqueous solution with 30% H_2O_2, Synth), and titanium tetrachloride, $TiCl_4$ (99.9%, obtained at IPEN's chlorination unit from titanium oxide catalyzed with graphite). In addition, HCl (37%, Sigma-Aldrich), Soybean oil (Liza), hexane (Synth), and ammonium hydroxide (30%, Synth) were utilized.

The following aqueous solutions were produced:

- HMTA solution with a concentration of 3 mol/L;
- Urea solution with a concentration of 3 mol/L;
- $NbCl_5$ solution dissolved in H_2O_2/H_2O;
- Titanium oxychloride solution with a concentration of 2.46 mol/L, obtained by controlled hydrolysis of $TiCl_4$.

The internal gelation precursor solution was prepared containing approximately 0.8 M of total metal ions, 1.76 M of urea, and 1 M of HMTA. Based on previous studies (obtainment of titanium oxide microspheres), the quantity of urea and HMTA used in the precursor solution was 1.19 M for both. The peroxo-complex method was utilized to obtain a stable solution containing Nb^{5+}, which involves the stabilization of $NbCl_5$ at low temperatures through the addition of hydrogen peroxide and water. At a temperature of 5 °C, the solutions containing the metal ions (Nb and Ti) were mixed with the solutions containing the organic agents (urea and HMTA).

This mixture was then introduced into a heated immiscible medium (Soybean oil at 90 °C) under constant stirring, thereby facilitating the gelation reaction and subsequent microsphere production. The emulsification/internal gelation process is depicted schematically in Figure 1. These microspheres were then separated from the immiscible medium and subjected to a series of washing and hydrothermal treatments, aimed at extracting the organic phase. Thereafter, the microspheres were dried in air for 24 hours, followed by a 24-hour heating period at 110 °C in an oven. The final step involved calcination at 550 °C for 60 minutes under an argon flux[12] at a heating rate of 1 °C per minute.

After the calcination stage at 550 °C, the microspheres were analyzed for their crystalline structure by X-ray diffraction (SmartLab SE conditions, Rigaku), morphology by scanning electron microscopy (SEM Tabletop TM3000, Hitachi), and for their specific surface area and porosity by N_2 adsorption/desorption (ASAP 2020, Micromeritics).

The employment of this methodology resulted in the synthesis of microspheres of Nb_2O_5 (Nb-p) and a mixture of these two ions, in Nb/Ti mol ratios of 93/7 and 81/19, respectively. These two molar ratios were defined by analyzing the phase equilibrium diagram of the Nb_2O_5-TiO_2 system[13]. Titanium oxide microspheres were prepared in a similar manner, but without the use of H_2O_2 and with a calcination temperature of 600 °C for 1 hour.

3. Results and Discussion

The micrographs obtained by SEM analysis of niobium oxide microspheres calcined at 550 °C demonstrated regularity in their geometry, accompanied by slight deformation of their morphology, as illustrated in Figure 2. This finding suggests that the gelation reaction occurred satisfactorily and that the washing and extraction procedures did not result in alterations to their morphology. However, it has not yet been possible to eliminate the cracks formed during the drying and calcination stages.

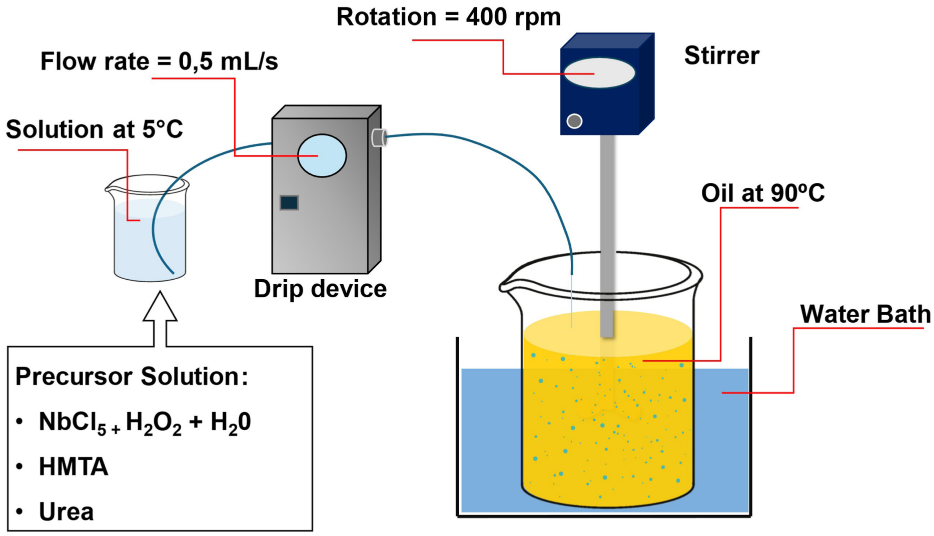

Figure 1. Schematic of the system employed for the production of microspheres by emulsification/internal gelation.

The process for obtaining TiO_2 microspheres from titanium tetrachloride has already been successfully developed in the CECTM/IPEN laboratories and has been described in detail in another publication[14]. Figure 3 shows some TiO_2 microspheres developed in this work, calcined at 600 °C, without cracks, deformations in apparent sphere shape, or agglomeration.

As illustrated in Figure 4, the microspheres obtained from the mixture of Nb and Ti chlorides (Nb81 and 93) exhibited numerous cracks and fractures, which resulted in the complete loss of their spherical morphology. Further studies are necessary to identify the causes of these phenomena and to develop modifications to the process that would eliminate them, both in the pure niobium oxide microspheres and in the mixtures. However, the method used to obtain microspheres by emulsification/internal gelation from Nb and Ti chlorides has proven to be initially viable.

For the X-ray diffraction analysis, the calcined microspheres were ground in a mortar, and the diffractograms shown in Figure 5 were obtained. For the peak investigation and phase determination, Eva software (Bruker, 4.2 version) and PDF database (2003) were used. As predicted based on the calcination temperature, the pure microspheres, Nb-p and Ti-p, exhibited the spectra of the crystalline phases orthorhombic Nb_2O_5 (PDF #71-0336) and anatase (PDF #71-1166). The Nb-rich mixture (Nb93) exhibited a crystal structure consistent with Nb_2O_5, indicating that the Ti atoms entered the Nb_2O_5 crystal structure and replaced the Nb atoms (substitutional solid solution).

Conversely, the Nb81 mixture exhibited an amorphous structure at the calcination temperature employed (550 °C/1 hour), suggesting that the quantity of Ti atoms exceeds the limit required for substituting Nb in its crystal lattice. This phenomenon hinders the process of crystallization within the preexisting crystalline structure, thereby preserving the amorphous gel structure. It can be deduced that at elevated temperatures, an intermediate phase of $(Ti\text{-}Nb)O_x$ will emerge in this specific mixture ratio.

The N_2 gas sorption analysis was employed to determine the specific surface area using the BET method, as well as the pore volume, distribution, and average pore size (BJH).

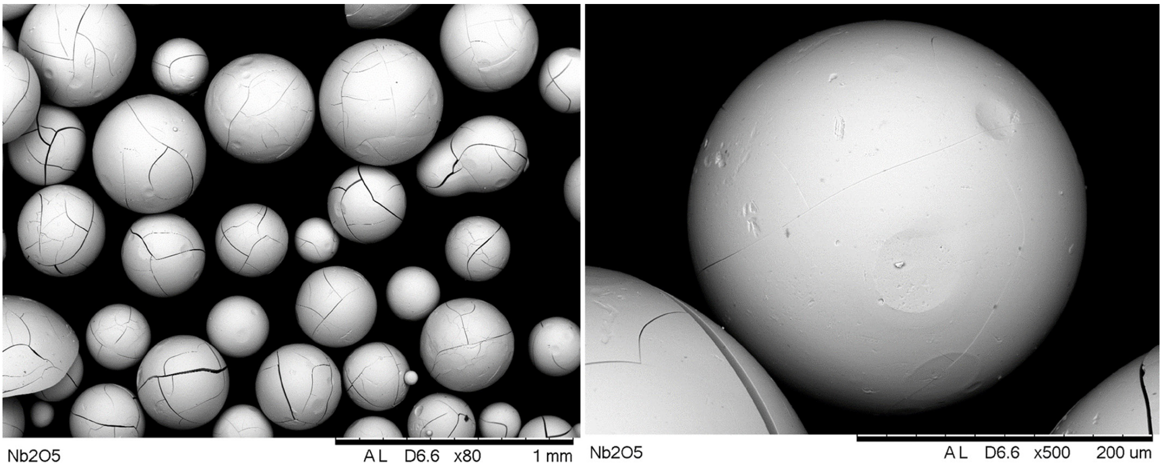

Figure 2. Niobium oxide microspheres (Nb_2O_5) calcined at 550 °C.

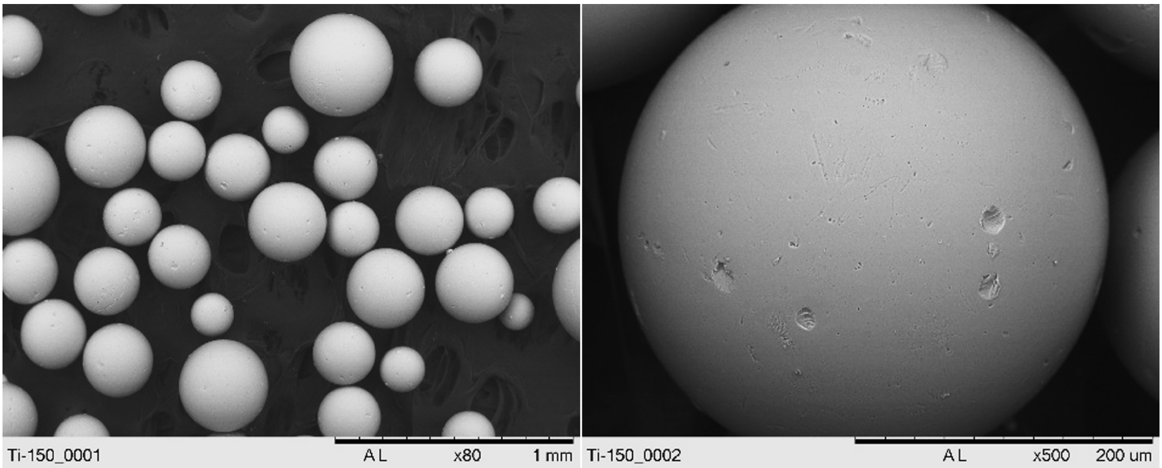

Figure 3. TiO_2 microspheres calcined at 600 °C.

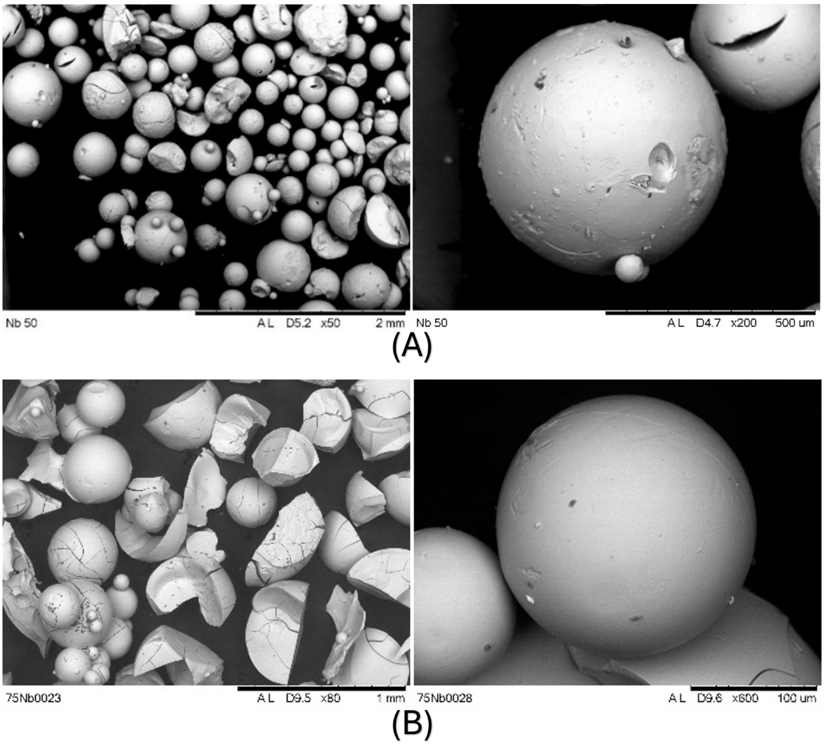

Figure 4. Scanning electron micrographs of the microspheres of the mixtures of niobium and titanium oxides after calcination, where (A) refers to sample Nb81 and (B) to Nb93.

The adsorption/desorption isotherms are shown in Figure 6, while the calculated values of specific surface area, pore volume, and average pore size are described in Table 1.

The adsorption curves obtained exhibited a shape analogous to type IV isotherms, as classified by the IUPAC. This characteristic is typically attributed to mesoporous materials. The hysteresis observed in the Nb-p and Nb93 samples, classified as type H1, is commonly associated with materials possessing cylindrical pores, arranged in a regular or organized three-dimensional network. However, it is also linked to a minor population of ink-bottle shaped pores, where the size of the cavity is comparable to that of the neck[15,16].

In contrast, the Ti-p and Nb81 samples exhibited comparatively more intricate hysteresis, consistent with type H2, attributed to a network of pores with ink-bottle shape and a wider variety of neck and cavity sizes. In the case of pure titania microspheres, this characteristic manifests as a subtle network of pores with narrow entrances and relatively uniform interiors. In the second case, the complexity of the mesopores present may be more intricate, exhibiting significant variations in size between the pore interior and the necks (adjacent tunnels). This suggests the presence of both cavities with narrow entrances and spacious interiors, and the opposite, approaching almost cylindrical pores[15,16].

It has been observed that the specific surface area decreased with the addition of titanium when comparing Nb-p sample with the Nb93 and Nb81 mixtures, with the values being 78.1 m^2/g, 65.4 m^2/g, and 74.6 m^2/g, respectively.

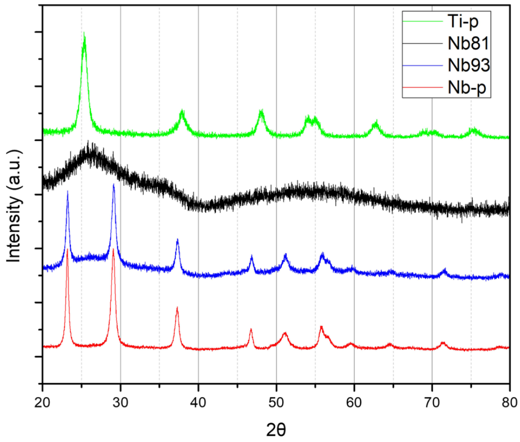

Figure 5. X-ray diffractogram of Nb-p, Ti-p microspheres and mixtures of Nb75 and Nb50 calcined at 550 °C for one hour.

Table 1. Calculated values for specific surface area (BET), pore volume (isotherm adsorption point at $P/P_0 = 0.95$) and average pore diameter (BJH desorption).

Sample	BET surface área (m^2/g)	Pore volume (cm^3/g)	Average Pore diameter (Å)
Nb-p	78.1	0.165	75.5
Nb93	65.4	0.199	104.9
Nb81	74.6	0.098	40.8
Ti-p	39.8	0.094	68.5

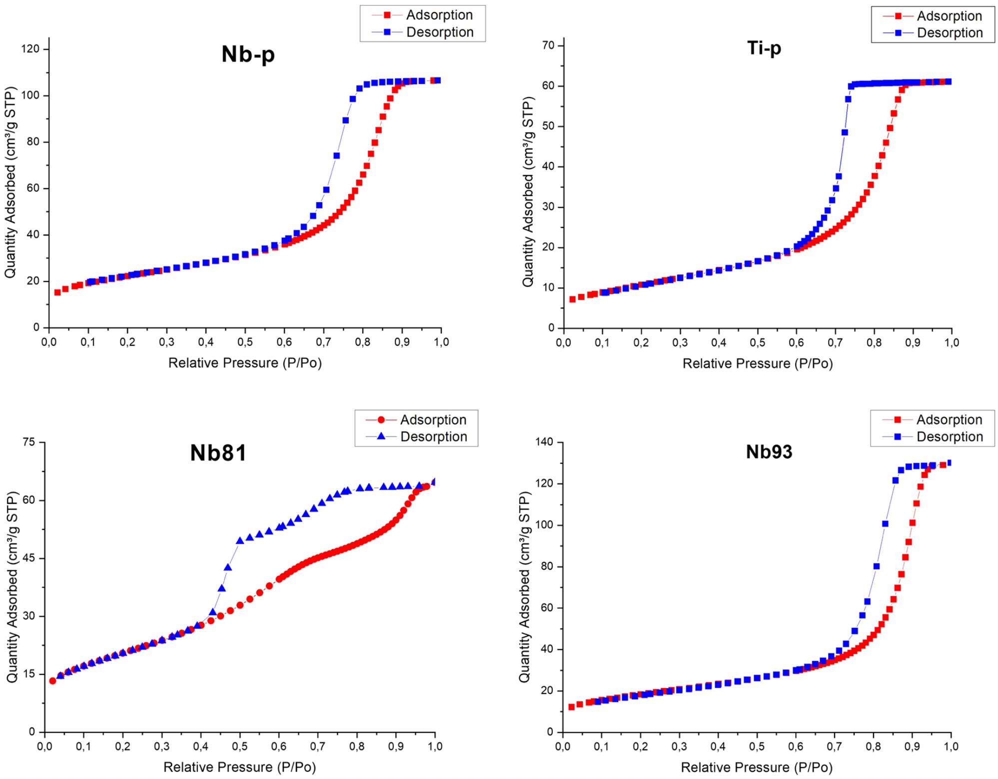

Figure 6. N_2 adsorption/desorption isotherms for Nb-p, Nb93, Nb81 and Ti-p.

The pure titania microspheres showed the smallest surface area among all, at 39.8 m^2/g. The significant disparity between niobium-titanium oxide-based microspheres, can be primarily attributed to the crystallization of the niobium-rich mixture, while the other remained amorphous. This phenomenon suggests a reduction in free surface area due to the growth and stabilization of the network into a well-defined crystalline structure[17].

A quantitative analysis of the pore size distribution graphs, presented in Figure 7, reveals those materials with higher pore volume exhibit mesopores with a broad size distribution and larger average diameters. This is exemplified by the Nb-p sample, which has pores ranging from approximately 40 to 120 Å, with an average diameter of 75 Å, and a volume of 0.165 cm^3/g, and Nb93, with sizes varying from 50 to 200 Å, with an average diameter of 104.9 Å and a pore volume of 0.199 cm^3/g.

The Nb81 sample exhibited the smallest average pore size (40.8 Å), with a volume of 0.098 cm^3/g. Through the pore size distribution curve, an additional indication of the high complexity of its pore network could be observed, as suggested earlier by the hysteresis shape. The distribution curve exhibited an intense peak at 35 Å, with a range extending from 40 to 110 Å, thereby supporting the hypothesis of a network comprising numerous narrow channels and cavities of varying sizes.

The Ti-p sample exhibited a pore volume of 0.094 cm^3/g, with an average diameter of 68.5 Å. It can be verified that its pore distribution is less extensive than the other microspheres obtained in the study, ranging from approximately 40 to 80 Å.

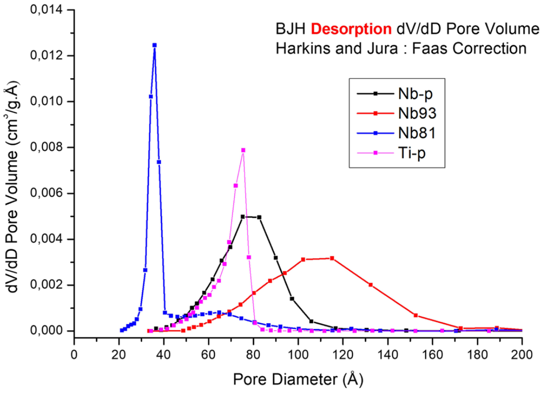

Figure 7. BJH pore distribution for Nb-p, Nb93, Nb81 and Ti-p.

4. Conclusion

The peroxide oxidation method has demonstrated significant advantages in chemical synthesis processes, particularly in the stabilization of metals such as niobium (Nb) in aqueous solutions. This method not only preserves the integrity of the metal species at low temperatures but also prepares the system for subsequent reactions, such as the formation of microspheres by internal gelation. The peroxide-induced stabilization is critical to prevent unwanted precipitation and maintain the metals in a soluble state, thereby facilitating process control and enhancing product quality.

In the internal gelling stage, achieving an optimal balance between gel formation kinetics and the mechanical strength of the material is fundamental. The selection of gelling agents and the concentration of total metals in the precursor solution play a pivotal role in the success of the process. The adjustment of these parameters can directly influence the uniformity of the microspheres, the absence of structural defects, such as cracks or fractures, and the efficiency of subsequent organic compound extraction processes. A primary challenge in synthesizing Nb_2O_5 microspheres and their mixtures with TiO_2 is the production of homogeneous materials, free of structural imperfections. The presence of cracks or fractures can compromise the mechanical and functional properties of microspheres, especially in applications where thermal resistance, chemical stability, and specific surface area are fundamental, such as catalysts or supports for chemical reactions.

Future studies could explore different ratios between niobium and titanium to investigate the synergistic properties of these metals in $(Nb\text{-}Ti)O_x$ mixed oxides. In addition, the optimization of the internal gelation process for industrial-scale up should consider the control of gelation time, the mechanical strength of the gel, and the efficiency of the extraction of organic agents. These enhancements are expected to ensure the reproducibility of the process on an industrial scale, thereby expanding its potential applications in fields such as catalysis, metal ion separation, and the support of biomaterials. Furthermore, the large-scale synthesis of microspheres with controlled properties has the potential to yield new technologies in areas where advanced materials are in high demand.

5. Acknowledgments

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6. References

1. Alves AR, Coutinho ADR. The evolution of the Niobium production in Brazil. Mater Res. 2015;18(1):106-12.
2. Bruziquesi CGO, Balena JG, Pereira MC, Silva AC, Oliveira LCA. Nióbio: um elemento químico estratégico para o brasil. Quim Nova. 2020;42:1184-8.
3. Jansto SG. Niobium Materials Technology in the Renewable Energy Sector. CBMM [Internet]. 2019 [cited 2025 Jan 9]:1-7. Available from: https://www.niobiumtech.cn/cn/-/media/project/cbmm-global/niobiumtech/apac/cn/pdf/energy/materialstechnologyintherenewableenergysector_8pages_pdf.pdf
4. Kang S, Miao R, Guo J, Fu J. Sustainable production of fuels and chemicals from biomass over niobium based catalysts: a review. Catal Today. 2021;374:61-76.
5. Liu Z, Zhao MC, Yin D, Zhao YC, Atrens A. Bio-functional niobium-based metallic biomaterials: exploring their physicomechanical properties, biological significance, and implant applications. Acta Biomater. 2025;192:1-27.
6. Peiter CC. Niobium as a strategic metal for Brazil. In: UNECE Resource Management Week 2021 - 12th Session of the Expert Group on Resource Management; 2021 Apr 26-30; Geneva. Proceedings. Geneva: UNECE; 2021 [cited 2025 Sep 1]. Available from: https://unece.org/sed/documents/2021/04/presentations/niobium-strategic-metal-brazil-carlos-peiter-centre-mineral-0
7. Rodrigues LA. Síntese de nanopartículas de óxido de nióbio hidratado via microemulsão inversa [thesis]. São Paulo: Universidade de São Paulo; 2009 [cited 2024 Sep 2]. Available from: http://www.teses.usp.br/teses/disponiveis/97/97136/tde-03102012-121612/
8. Santos AJ, Batista LMB, Martínez-Huitle CA, Alves APDM, Garcia-Segura S. Niobium oxide catalysts as emerging material for textile wastewater reuse: photocatalytic decolorization of azo dyes. Catalysts. 2019;9(12):1070.
9. Costa LL. Aplicação de nanotubos de titânia na fotodegradação de corantes [thesis]. Brasília: Universidade de Brasília; 2009 [cited 2024 Aug 4]. Available from: http://repositorio2.unb.br/jspui/handle/10482/4544
10. Falk GS. Síntese e processamento de pentóxido de nióbio e óxidos mistos de nióbio e titânio nanoparticulados e estudo de suas propriedades fotocatalíticas [thesis]. Florianópolis: Universidade Federal de Santa Catarina; 2017 [cited 2024 Oct 12]. Available from: https://repositorio.ufsc.br/handle/123456789/180557
11. Hunt RD, Hickman RR, Ladd-Lively JL, Anderson KK, Collins RT, Collins JL. Production of small uranium dioxide microspheres for cermet nuclear fuel using the internal gelation process. Ann Nucl Energy. 2014;69:139-43.
12. Xu R, Song J, Zhao S, Nie L, Deng C, Hao S, et al. The effect of washing process on the cracking of ZrO2 microspheres by internal gelation. J Am Ceram Soc. 2021;104(11):5489-500.
13. Choi SH, Kim TS, Ali B, Choi KS, Hyun SK, Sim JJ, et al. Reaction kinetics and mophological study of TiNb2O7 synthesized by solid-state reaction. Arch Metall Mater. 2017;62(2B):1051-6.
14. Oliveira GL, Andreoli M, Genova LA, Silva GP. Tratamentos alternativos para a eliminação de trincas em microesferas cerâmicas produzidas por gelificação interna. In: 23º CBECiMat - Congresso Brasileiro de Engenharia e Ciência dos Materiais; 2018 Nov 4-8; Foz do Iguaçu. Proceedings. São Paulo: Metallum; 2018 [cited 2024 Oct 12]. p. 1283-94. Available from: https://metallum.com.br/23cbecimat/anais/PDF/It41-008.pdf
15. Cychosz KA, Thommes M. Progress in the physisorption characterization of nanoporous gas storage materials. Engineering. 2018;4(4):559-66.
16. Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl Chem. 2015;87(9-10):1051-69.
17. Yan J, Wu G, Guan N, Li L. Nb2O5/TiO2 heterojunctions: synthesis strategy and photocatalytic activity. Appl Catal B. 2014;152-153:280-8.

Data Availability

The data supporting the conclusions of this study are available upon request to the corresponding author. At the time of publication, the data were undergoing organization, curation, and validation according to FAIR principles. After the completion of these procedures, the dataset will be deposited, made publicly available on the SciELO Data platform, and presented as an addendum.