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METHODS OF OBTAINING MAGNESIUM NANOSTRUCTURED ADSORBENT MATERIALS

BY

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Abstract. Researches in material oxides offers solutions in a variety of fields including environment, energy production and storage, biotechnology, medicine and healthcare, electronics, etc. Nanomaterials have concerned attention in recent decades due to their different enhanced properties, such as a large surface, particle size, optical or magnetic properties. To obtain oxide nanomaterials with good performance, the controlled shape of nanoparticles is very important. This paper outlines few methods for the preparation of nanoparticles as well as the advantages of using methods to obtain oxide materials. Conventional methods are still used in the industrial production of many oxide materials, however there is a growing demand for alternative routes to green synthesizes of oxide materials with superior properties. The main current methods of obtaining nanomaterials in the solid state are the sol-gel method, coprecipitation, hydrothermal.

Keywords: nanomaterials, sol-gel method, precipitation/ co-precipitation method, hydrothermal/solvothermal method.

1. Introduction

The creation of environmentally friendly products and processes has taken priority in recent years as concerns about climate change, water pollution,

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limited natural resources, human health, etc. have gained significant attention (Buema *et al*., 2021; Nutescu Duduman *et al.*, 2022). As a result, scientists have been creating several strategies to improve the synthesis of metals and metal oxides utilizing environmentally friendly technology. The synthesis of metal oxides and nanostructured metals using simple, effective methods has been thoroughly studied (Abinaya *et al.*, 2021; Harja *et al.*, 2022). The oxides have developed the consideration of several researchers in last decade due to their potential in different fields application (Ali *et al.*, 2016; Apostolescu *et al.*, 2023; Qi *et al.*, 2022; Wei *et al.*, 2022). MgO nanoparticle synthesis has received a lot of attention in the recent years due to its special characteristics, which include a high ionic nature, a simple crystal structure and stoichiometry, a large surface area, high reactivity due to the abundance of active sites, controllable particle size with different shapes, and the presence of numerous crystal defects on the solid surface (Ismail *et al.*, 2022, Li *et al*., 2019; Prado *et al.*, 2020). Magnesium oxide is the most interesting of them because it is inexpensive, stable, harmless, and environmentally benign (Balaba *et al*., 2023).

As a result, magnesium oxide was used in a lot applications for example: catalyst supports, ceramics, antibacterial applications, toxic waste depollution, paint, adsorbent, etc. (Dhal *et al*., 2015; Moulavi *et al*., 2019; Yan *et al.*, 2013).

Commercial MgO powder, a metal adsorber that is frequently produced by the thermal decomposition of $MgCO_3$ or $Mg(OH)_2$, has limitations, including a low specific surface area, irregular shape, and large particle size (Balaba *et al.*, 2023). Generally, various kind of synthesis methods are employed to obtaining MgO nanoparticles such as sol-gel, coprecipitation, electrochemical, vapor deposition, hydrothermal microemulsion, etc. The sol-gel technique is one of the most recognized among these techniques (Mastuli *et al*., 2014). MgO nanoparticles for a number of reasons, including their simple manufacturing procedure, excellent product yield, and low reaction temperature needs. Additionally, the sol gel approach provides a cheap way to obtain MgO with a small size distribution and a significant surface area, which is crucial to resolving the issue of low reactivity and catalytic activity.

2. Methods for obtaining nanostructured oxide materials

Conventional methods are still used in the industrial production of many oxide materials; however, there is a growing demand for alternative routes to synthesize oxide materials with superior properties compared to those presented by materials obtained by conventional methods. The need for alternative synthetic routes for oxide materials arose due to problems related to the un-homogeneity of the products obtained; the incorporation of chemical impurities during repeated grinding and heating operations.

To obtain oxide nanomaterials with good performances, the controlled growth of nanoparticles is very important. The most used approaches for the synthesis of oxide nanomaterials are those in the liquid phase, such as: the sol-gel method, precipitation/coprecipitation method, hydrothermal/solvothermal method. Table 1 summarizes the methods, recommended in literature for the synthesis of magnesium oxide.

Table 1
The methods for the synthesis of magnesium oxide

Precursors	Synthesis method	Conditions of synthesis	Materials obtained	References
$Mg(NO_3)_2 \cdot 6H_2O$ urea, ethylene glycol, and ethanol	Chemical Synthesis	110-120°C for 12 h 5 h at 450	MgO foils	Dalvand *et al.*, 2020
$Mg(NO_3)_2 6H_2O$ $Fe(NO_3)_3$ $9H_2O$ NaOH polyetilen glycol - etanol	Hydro-thermal synthesis	stirred at 50-60^{0}C, NaOH was added dropwise, calcination at 550^{0}C	MgO, Fe_2O_3 Fe_2O_3–MgO	Sahoo *et al.*, 2020
$Mg(NO_3)_2 6H_2O$ NaOH	Precipita-tion	0.1M $Mg(NO_3)_2$ stirred 2 h at 20°C. Calcined 4 h at 500^{0}C	MgO nano-particles.	Park *et al.*, 2006.
$Mg(NO_3).6H_2O$ $C_6H_{12}N_4$	Copre-cipitation	1M solution of $C_6H_{12}N_4$ and 1 M $Mg(NO_3)_2$ stirred 10 min. at 20°C	MgO nanoparticles	Nemade and Waghuley, 2014
$Mg(NO_3)_2 6H_2O$ sodium hydroxide ammonia solution	Sol-gel method	0.2 M $Mg(NO_3)_2$ 0.4 M NaOH was added and sonication. Calcination at 500^{0}C for 4 h	Synthesis of hierarchically structured MgO	Tamilselvi *et al.*, 2013
$Mg(NO_3)_2$ Extracts from leaves of Pisidium guajava *Aloe vera*	Sol-gel method	1 mM of $Mg(NO_3)_2$ 90 ml of Pisidium leaf extracts 100 mL of 1 mM NH_3 stirred 30 min., calcined at 600^{0}C for 2 h	Green synthesis of MgO nano-particles	Umaralikhan and Jaffar, 2018
$MgCl_2$ aqueous solution ethylene glycol	Hydrolysis Condensati on	110º C for 12 hours in continuous stirring. Calcined at 450 and 650ºC for 5 hours	Hydro-micro magnesium sheets	Selvamani *et al.*, 2011

The sol-gel method (Fig. 1) is currently the most investigated chemical method of synthesis because it can be applied to a wide range of materials (Nutescu Duduman *et al.*, 2018), being a versatile process used for the synthesis of various oxide materials and allowing the possibility to control the shape, texture, dimensions and distribution particle sizes (Duduman *et al.*, 2018; Moulavi *et al.*, 2019).

The sol-gel method facilitates the preparation of the nanomaterials in different forms (powders and films). In addition, it is very convenient for the production of nanocomposite materials in which different phases can be well dispersed in an inorganic matrix, such as the doping of titanium dioxide with different metal or non-metal ions.

The principle of the sol-gel method consists in obtaining metal oxides through hydrolysis and polycondensation processes of solutions of inorganic or organic precursors with gel formation.

The oxidic materials are formed by heat treatment of gels at relatively low temperatures compared to the classical route of solid phase reactions.

This method also has several advantages over other methods, such as: allowing impregnation or coprecipitation, which can be used to introduce dopants, the product has a good homogeneity and purity, the process can be conducted at low temperatures, the process provides control over multiphase systems stoichiometry, shape, dimensions and physicochemical properties, compounds with high specific porosity are obtained (high porosity), it can be done with a relatively low energy consumption due to the low synthesis empires.

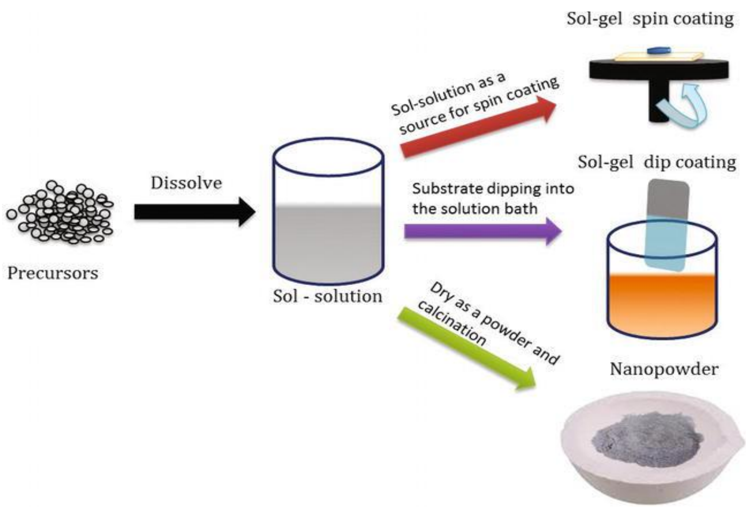

Fig.1 – Schematic representation of the sol gel method
(Thiagarajan *et al.*, 2017, reproduced under the terms and conditions of the Creative Commons Attribution 3.0 License).

The sol-gel method is a technique for improving the physicochemical and electrochemical properties of nanocrystals. It is a simple process of nanoparticle synthesis at ambient temperature under atmospheric pressure, and does not require complicated equipment.

Co-precipitation involves reaching supersaturation conditions of the cation solution (Fig. 2). This fact can be achieved simply by choosing the appropriate pH value. The precursors of the obtained solid are the hydroxides of the metals in the cationic sheets, and the pH chosen depends on the nature of the cations and their ratio.

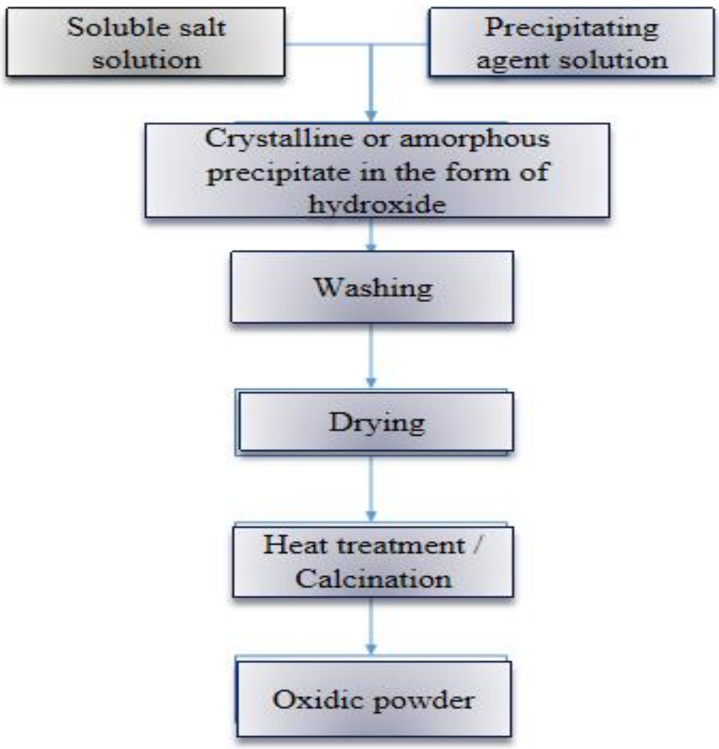

Fig. 2 – Schematic diagram of the process of obtaining oxide materials by coprecipitation.

For a uniform product, coprecipitation at low supersaturation is chosen. The most commonly used conditions are: pH = 7 – 10, T = 333 – 353 K, low concentration of reagents and slow mixing of the two solutions.

Hydrothermal synthesis is a widely used method for the production of nanoparticles in the ceramic industry and is normally carried out in steel vessels, called autoclaves, under controlled pressure and temperature, with the reactions taking place in aqueous solutions (Fig. 3). The solvent used is not only the reaction medium, but also helps to maintain a high pressure. The temperature and amount of solution introduced into the autoclave largely determine the internal pressure produced.

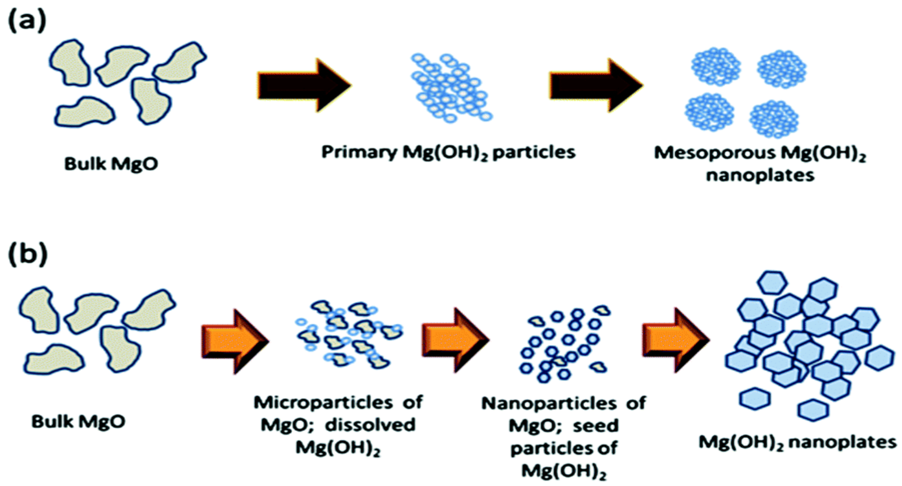

Fig. 3 – Schematic diagram of the process of obtaining oxide materials by hydrothermal synthesis (a) conventional hydrothermal synthesis and (b) microwave-hydrothermal synthesis.

This method ensures high homogeneity, high purity, crystal symmetry, metastable compounds with unique properties and narrow particle size distributions. The technical parameters of the hydrothermal synthesis, such as the solvent used and the working temperature, can directly affect the crystalline phase that is obtained, the morphology of the nanoparticles, as well as the degree of crystallinity, all of these parametrically influencing the performance of the oxide, hydrothermal processes, the typical synthesis is carried out at temperatures large enough, agglomerated nanocrystals are formed. In order to improve the properties of the final product, different reaction conditions, precursors, catalysts were used, and in some cases even stabilizing agents were added to prevent agglomeration of nanoparticles.

3. Conclusions

Considering the importance of the methods of obtaining nanostructured oxide materials, in order to obtain oxide nanomaterials with good performances, especially for adsorption and/or catalytic applications, the controlled growth of nanoparticles is very important.

The advantages of using the method of obtaining nanostructured oxide materials are:

- Synthesis of fine oxide powders, with morphology and particle size well controlled by precursor particle size and working conditions;
- Compounds with large specific surfaces are obtained (high porosity);
- It can be achieved with a relatively low energy consumption due to the low synthesis temperatures;

- The ability to carry out the synthesis at low temperatures; the variety of crystal sizes and shapes produced, depending on the initial mixture's composition and the temperature and pressure of the reaction; the high degree of crystallinity and high purity of the material produced;

It is an easy and environmentally friendly method because it doesn't require the use of organic solvents or extra product processing (grinding and calcination).

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METODE DE OBȚINERE A MATERIALELOR ADSORBANTE NANOSTRUCTURATE DE MAGNEZIU

(Rezumat)

Cercetările în domeniul oxizilor metalici oferă soluții într-o varietate de domenii, inclusiv mediul înconjurător, producția și stocarea energiei, biotehnologie, medicină și asistență medicală, electronică, etc. Nanomaterialele au atras atenția în ultimele decenii datorită proprietăților lor îmbunătățite, cum ar fi suprafața mare a particulelor, dimensiuni reduse, proprietăți optice sau magnetice deosebite. Pentru a obține nanomateriale oxidice cu performanțe bune, forma controlată a nanoparticulelor este foarte importantă. Această lucrare prezintă câteva metode de preparare a nanoparticulelor, precum și avantajele utilizării metodelor de obținere a materialelor oxidice. Metodele convenționale sunt încă utilizate în producția industrială a multor materiale oxidice, cu toate acestea, există o cerere din ce în ce mai mare pentru rute alternative de sintetiză a materialelor oxidice cu proprietăți superioare prin metode prietenoase cu mediu. Principalele metode actuale de obținere a nanomaterialelor în stare solidă sunt metoda sol-gel, coprecipitarea, metoda hidrotermală.