A REVIEW OF RECENT DEVELOPMENT OF THE SOLVENT-DEFICIENT METHOD

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Abstract: The challenges of modern society and the requirements for high-tech materials have led to a new stage in the development of chemical synthesis methods. This stage is demanding a reliable, controllable, and green approach to the production of necessary materials. One of the recently developed approaches for metal oxide nanoparticles synthesis is the solvent deficient method. A cutting edge of this synthetic method is a synthesis with increased control throughout chemical transformation resulting in optimal conditions for materials production. As a result, oxide nanoparticles are produced fast, environmentally friendly, cost-effective, and with low energy consumption. On the other hand, a complex reaction mechanism is presenting a challenge for reliable kinetic studies. The present review follows the recent trends in the development of the solvent deficient method concerning the binary, ternary, and complex metal oxides. Special attention is given to considering approaches responsible for desirable mechanisms of catalytic applications. In future development, the reported synthesis method is expected to be employed in a high entropy oxides formation. Due to simple preparation steps, it will be possible to automatize the reaction procedure and investigate a large number of possible compositions which is imperative for new complex materials. Finally, precursors heating could be transformed from conventional to microwave. Solvent-deficient method deals with precursors sensitive to microwave irradiation which could ensure rapid heating and transformation to desirable oxide nanomaterials.

Keywords: solvent-deficient synthesis, nanoparticles, metal oxides.

1. INTRODUCTION

The presence of nano- and mesoscale pores in metal oxides plays a critical role in intensifying the chemical and physical reactivity of nanoparticles. Such materials have potential applications in catalysis, adsorption, sensors, gas purification, as well as in solar cells [1–4]. During the past few decades, the synthesis of metal oxide nanoparticles has fascinated the interest of scientists all over the world following the general trend of the nanotechnology market. This development resulted in several approaches to various environmental issues. Following the principles of green chemistry, new reactions and methods are identified as suitable for environmental pollution reduction [5]. These approaches are designed to be uncomplicated, time and energy effective, and environmentally friendly. Newly designed synthesis methods should also be carried out at lower temperatures by using non-toxic solvents. According to Stavis et al. [6], the most profitable innovations in nanoparticle manufacturing are minimizing heterogeneity in processes of synthesis, stabilization, and functionalization. Among other consequences, this reduces the need for purification that decreases yield, and generates waste.

The majority of current approaches to metal oxide nanoparticle synthesis can be classified as solid-state, solution-phase, and vapor-phase methods [7]. However, no synthesis technique is ideal for every

application and there are substantial differences in resulting nanomaterials characteristics [8]. On the other hand, industrial production of metal oxide nanomaterials is very often limited by the demanding equipment and procedures necessary for the synthesis.

The solvent-deficient (SD) synthesis method (Figure 1) first reported by Woodfield and Smith et al. [9] proved to be successful for the synthesis of a vast range of oxide nanomaterials. These include oxides from almost every semi-metal and transition metal group as well as a few from the lanthanide group. In short, the SD method includes grinding a hydrated metal salt (mostly a nitrate salt) with bicarbonate (mainly NH_4HCO_3) for up to 30 minutes to form a precursor. The precursor is further rinsed with water or untreated before being annealed at rather low temperatures for up to 3 hours. No, or limited addition of solvent is added during synthesis. The SD method is similar to the co-precipitation method [10], with the difference that no, or limited amount of additional solvent is added. The resulting solvent-deficient surrounding is inducing increased crystallinity and a mesoporous nature of the products. The method is swift, requiring not many steps and a total of 2 to 5 hours. The technique is additionally having a limited environmental burden, by avoiding the use of toxic solvents.

Metal-nitrate(s)-hydrate NH_4HCO_3

Mixing: 20-30 min Rinsing

Calcination: 60-180 min 250 - 550 °C

Metal-oxide nanopowder
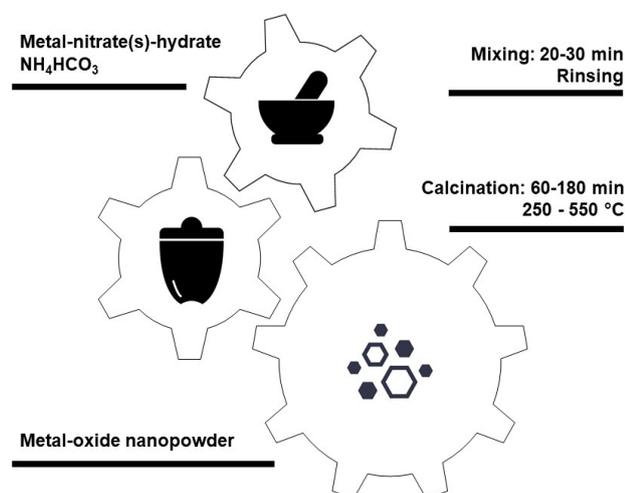
Figure 1. General preparation scheme for the solvent-deficient synthesis

Within this paper, we outlined the procedure of the solvent-deficient method using our knowledge of its mechanism. Additionally, we summarize the range and nature of nanomaterials it has produced up to now and drafts future perspectives on this method's application and development.

2. SOLVENT-DEFICIENT PROCESS STEPS: AN OVERVIEW OF PLAUSIBLE MECHANISM

SD method consists of only a few different steps. The metal nitrate hydrate and ammonium bicarbonate are initially ground together, forming the mixture of metal compounds and NH_4NO_3 as given in Eq.1. Metal nitrates in their hydrated forms are suitable as the precursor since chlorine may remain as an impurity in the oxide product when metal chlorides are used as the precursor. The water of crystallization in the metal salts acts as a solvent, enabling the dissociation of the reagents and release of CO_2 during bicarbonate decomposition. Additionally, this water reduces the necessary grinding time. The moles of bicarbonate are equivalent (or close to equivalent) to the moles of anion originating from the metal salt. This ratio is set to ensure the complete formation of precursor molecular structures. The grinding time is set to 20 to 30 minutes. This period is based on the time necessary for the complete removal of the evolving and trapped gas.

$$M(NO_3)_x \cdot yH_2O + xNH_4HCO_3 \xrightarrow{\text{Grinding}} \text{Precursor(s)}$$

$$\xrightarrow{\text{Optional rinsing}} \text{Rinsed precursor} \xrightarrow{\text{Annealing}} \text{nano } M_aO_b$$

$$(1)$$
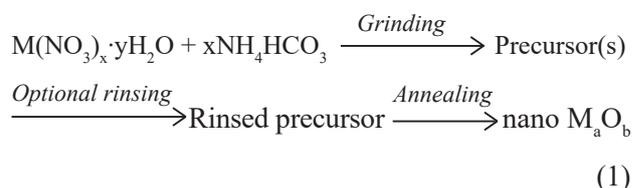
During the grinding of the precursor, the complex molecular structures are formed around the embedded spectator molecules/ions such as H_2O, NO_3^-, NH_4^-, etc. They are further forming a template for the SD synthesis whose removal during rinsing and annealing leads to oxide nanoparticles with a mesoporous nature. The metal nanoparticles formed after the annealing of the precursors without the rinsing step in many cases results in larger grains. The reason for this is the mixed metal hydroxide/oxy-hydroxide/carbonate/nitrate and NH_4NO_3 byproducts, formed during the grinding reaction. The rinsing step is set to remove ammonium nitrate, the soluble by-product formed during grinding. Ammonium nitrate is soluble in water and this step in certain cases ensures a small crystallite size. The rinsing of the precursors also results in the replacement of the NO_3^- ligand and H_2O by the OH^- ions. In many precursor systems, this drastically decreases the grain and crystallite size. The

annealing temperature for all of the previously reported oxides is reasonably low, enabling preservice of nanoparticles, in most cases. The annealing time is for all the systems previously examined set to a frame of one to three hours.

The absence of toxic solvents, energy efficiency, short synthesis time, high yield, and uncomplicated setup is making the SD method applicable for the synthesis of many different oxide materials.

3. APPLICATIONS

3.1. Binary metal oxides

Aluminum oxide is one of the most investigated materials from the point of SD synthesis and doping. Due to a simple and controllable synthesis, low price, and nano- and mesoporosity, this material is found to be suitable as catalyst support. Smith et al. [11] have followed γ-Al_2O_3 nanoparticles' phase progression in an SD environment. This simple but amazing material is found to emerge from the boehmite phase with temperature-related structural defects. The diffusion-controlled transition from boehmite to γ-Al_2O_3 is additionally followed by Ivas et al. [12]. This research followed up on γ-Al_2O_3 densification and crystal growth controlled by calcination temperature. The gradual transformation from boehmite to nano-sized Al_2O_3 is followed by x-ray diffraction analysis (Figure 2). The calculated crystallite size (by Scherrer equation), and specific surface area indicate the nanocrystalline nature of the samples (Table 1).
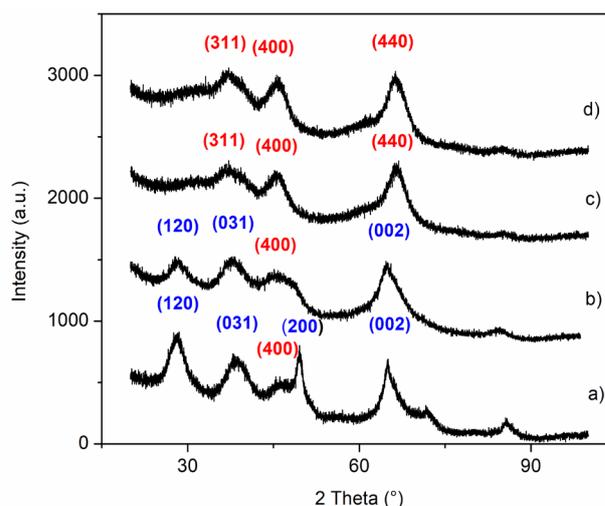
Figure 2. *XRD of the Al_2O_3 powders prepared by solvent deficient method and calcined at 300 (a), 400 (b), 500 (c), and 600 °C (d) with marked peaks of γ–Al_2O_3 (red) and AlOOH (blue) phase. Chemical transformation is found to be gradual and results in nano-sized powder [12]*

Mesoporous γ-Al_2O_3 is widely used as a support in catalytic applications due to its high surface area, acid-base characteristics, large pore volume, and thermal stability. To improve the thermal stability of γ-Al_2O_3, dopants such as silica, and lanthanum are often introduced. The usability of γ-Al_2O_3 as catalyst support depends on its favorable combination of thermal, textural, structural, and chemical properties [13]. The mechanism of γ-Al_2O_3 thermal stabilization by dopants is still not well understood but recently there is a new approach based on SD synthesis. Smith et al. [14] investigated alumina doping

Table 1. *Crystallite size, specific surface area, and phase structure of nanocrystalline boehmite (b) and γ–Al_2O_3 (γ) annealed at various temperatures [12]*

Sample	Annealing temperature / °C	Crystallite size / nm	Specific surface area / m²g⁻¹	Crystal structure*
a	300	2.46	279.56	b + γ
b	400	1.51	336.53	b + γ
c	500	1.80	311.31	γ
d	600	1.91	245.49	γ

*(b): nanocrystalline boehmite, (γ): γ-Al_2O_3

with the La^{3+} to stabilize the γ-phase at higher temperatures. The applied one-pot SD method resulted in a radical reduction of La-doped γ-Al_2O_3 nanoparticles preparation time (3h vs. 3 days for impregnation methods), and a high level of La utilization. La is found to stabilize the γ-Al_2O_3 phase by 100 °C. The proposed mechanism includes strong La to alumina interaction (La enveloping by the Al_2O_3 lattice) during the γ-to-α transition. The SD method is here again proved to be more environmentally benign than the impregnation method for La-doped γ-Al_2O_3 nanoparticles preparation. Interesting effects of the SD environment are also found in the case of Pd-doped γ-Al_2O_3 [15]. It is determined that Pd-Al_2O_3 catalysts synthesized by an SD method provide 20% higher hydrogen release capability in comparison to conventional Pd-Al_2O_3 catalysts. The chemical reaction catalyzed was the dehydrogenation of four distinct N-heterocyclic composites at or below 250 °C. The catalyst activity loss, for up to five consecutive runs, is found negligible, which is explained by the SD environment that successfully restricts well-dispersed Pd mobility within contiguous alumina particles. In another research [16] mesoporous Pd-Al_2O_3 catalysts synthesized by an SD method are found to be active and selective for the dehydrogenation of liquid organic hydrogen carriers. Within this study, it is found that the healing of boehmite-like stacking-fault defects is responsible for the existence of smaller Pd particles with higher dispersion. This results in better dehydrogenation capability as compared to the other studied catalysts. The Al_2O_3 is found to limit the Pd particle growth which adds to the exceptional stability of the catalysts.

Another investigated system prepared by the SD method is the mesoporous Cu-Al_2O_3 catalyst [17]. The reaction catalyzed by this system was hydrodeoxygenation of furfural to 2-methyl furan. The optimized catalyst exhibited improved reactivity, selectivity, and stability in furfural hydrodeoxygenation. Discovered unique pore architecture, and also the synergistic outcome of enhanced Cu accessibility, co-existence of Cu^0/Cu^+ states, and robust metal-support interaction are found to add to the catalyst's superior activity and stability. The authors here concluded that the strong metal-support interaction induced by the water scarcity during synthesis increased the stability of the catalyst. The altering of the calcination temperature proved to be one of the main factors influencing the structure and the activity of the catalyst.

The found unique SD synthesized catalyst capability could be extended to various Cu-promoted hydrogenation and dehydrogenation reactions. The SD method as a whole can be potentially applied to other supported metal catalysts. In that regard, simple temperature tuning during synthesis could simply and strongly influence the structure-activity relationship. Small particle size, co-existence of different oxidation states, and lattice vacancies in CuO prepared by the SD method could be interesting not only to catalysis but also to the field of nanomagnetism [18] where the nature of the magnetic state is still not elucidated.

Recent application of the SD method is also recorded in the paper dealing with toluene oxidation under ozone over mesoporous MnO_x/γ-Al_2O_3 catalyst [19]. Catalytic activity is found favorable and the SM method is designated as an advanced method for meso- and nano-catalysts synthesis.

A solvent deficient environment is also successfully applied in the preparation of a mesoporous network of amorphous α–$Ni(OH)_2$. The SD method provided the uniform pore size distribution, large pore volume, and large surface area to the $Ni(OH)_2$ samples. The resulting material showed excellent electrochemical performance [20].

The effect of the rinsing step was inspected during SD synthesis of mesoporous Co_3O_4 nanoparticles for electrochemical energy storage. The rinsing step is found to provide a special effect resulting in the crystallite size and grain size decrement. The good electrochemical performance of synthesized cobalt oxide nanoparticles made the material a potential candidate as electrode material in energy storage appliances. The capacity retention for Co_3O_4 samples is found to be 77.8% and 82.1% for untreated and rinsed precursors, respectively [21].

Kore et al. [22] investigated the synthesis of NiO nanoparticles using the SD approach. By changing the reagent ratio of nickel nitrate and ammonium bicarbonate (mole ratio from 0.5 to 4) they achieved a measurable effect on the formation of NiO nanoparticles. Particle size is found to be larger for the lower content of ammonium bicarbonate. Furthermore, the authors noted the shift in electrochemical performance (the specific capacitance) achieved by the reagent ratio change. As reported, equal moles of ammonium bicarbonate to that of the oxidation state of a nickel nitrate salt are found favorable for complete utilization of reagents and produced NiO performance as an electrode

material for supercapacitor application. Nanoparticles of NiO were also a point of interest for other authors. Farook et al. [23] quite recently reported that the application of various catalysts (Ni/CeO_2, Ni/CeO_2-La_2O_3, Ni/CeO_2-ZrO_2) prepared by the SD method increased the hydrogen production yields from the steam gasification of furniture waste. The authors recommended the SD method as an economical method for the preparation of lanthanum and ceria-based catalysts, after being compared to those commercially available catalysts. They pointed out that the SD method opens a new route for biohydrogen generation in real applications enabling large-scale efficient renewable energy integration.

SD method is also identified as the fastest and simplest route to synthesizing ferrihydrite. Prepared crystallites are determined to be 2−6 nm in diameter further aggregating into mesoporous, high surface area agglomerated structures that are found to be candidates for many adsorption applications [24]. The SD synthesized ferrihydrite is already utilized for successful arsenic removal [25] with the authors noting that different batches produced using the SD method yielded materials with surface areas varying from 192 to 329 m^2g^{-1}. Rinsing was also performed during the synthesis of mesoporous Fe_2O_3 nanoparticles [26]. The performance of the unrinsed and rinsed specimens is defined using chronopotentiometry, cyclic voltammetry, and electrochemical impedance spectroscopy. The results are indicating a positive influence of rinsing on specific capacitance, energy density, and power density. Additionally, it is noteworthy to mention prolonged cyclic stability for Fe_2O_3 obtained from untreated and rinsed precursors. Even before this research, Fe_2O_3 was prepared by the SD method in the form of Fe_2O_3/Carbon black nanocrystals as a catalytic substrate for the phosphidation

reaction [27]. The resulting iron phosphide catalyst is successfully utilized for the high-efficiency hydrogen evolution reaction. The authors also showed that SD synthetic method is universal for many other transition metal phosphides such as CoP/C nanocrystals and Ni_2P/C nanocrystals. Due to a high-yield, low-cost and scalable strategy, the SD method is found to open a new way to developing superior hybrid catalysts for the hydrogen evolution reaction.

The in-depth analysis of the SD method is performed following CeO_2 synthesis [28]. The reaction mechanism and kinetics of CeO_2 synthesis using the SDM are found to be marked by the four observed stages. The best description of the first three reaction stages is done by the Nth order reaction model, while the last stage was best explained by the nucleation and growth model. The suggested mechanism indicates a complex synthesis with several alongside reactions, out setting even at room temperature. This first SD method mechanism and kinetics study did not cover the influence of the kinetic parameters on the particle size. CeO_2 was also interesting for doping purposes. Gadolinium-doped cerium oxide (GDC) synthesized using the SD method is investigated for its sinterability and electrical properties using the powder and cold sintering process [29]. The low-temperature processing within the SD method is found not to cause significant phase segregation along grain boundaries. As a result, there is an increase in grain boundary conductivity that is consistent with the grain boundary microstructure. Apart from the above, it is noteworthy to mention the synthesis of nanocrystalline Co_3O_4 and Mn_3O_4 by SDM for thermodynamic studies [30].

The recent development is also made in La_2O_3 [31] and N-ion doped ZnO [32] synthesis. Especially interesting is the latest one. Notably, in this case,

Figure 3. Photography of N-ion doped ZnO calcined at (from left to right) 300, 400, 500, and 600 °C

nitrogen doping was provided from the ammonium nitrate already present within the precursor mixture. During ammonium nitrate thermal decomposition, an unfavorable thermal exothermic effect is confirmed to enforce nanoparticle agglomeration, but also nitrogen incorporation into ZnO. This is also visually confirmed (Figure 3) with the note that the orange color of ZnO is coming from the incorporated nitrogen, and its intensity is quantitative dependent. Produced N-ion doped ZnO is found to possess superior photocatalytic activity towards methylene blue degradation (Figure 4).
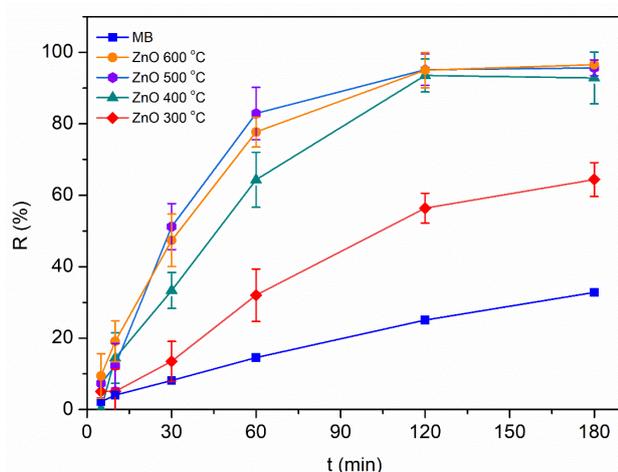
Figure 4. *Photocatalytic activity (R%) of N-ion doped ZnO samples on methylene blue degradation [32]*

3.2. Ternary and complex metal oxides

Ternary metal oxide nanostructures are found to be of fundamental scientific interest with a broad range of technological applications [33] and production in a variety of sizes and shapes. Though, their production needs to be favorable from the point of environmentally friendly protocols and exactly described regarding the growth mechanisms involved. They are found to be superior over the counterpart binary metal oxides for many chemical [34] and energy-related applications [35]. SD method proved to be reliable for ternary metal oxides production. So far, synthesized nanostructures included spinel ferrite $MgFe_2O_4$ individual nanospheres. Doping with Mg induced the existence of two kinds of defects in the spinel ferrite: vacancy defect and local defect clusters. As a result, increased concentration of surface hydroxyl group enhanced materials adsorption ability for As(V) [36].

The ternary $NiFe_2O_4$ nanoparticles were also synthesized by the modified SD method. The modification included a change in the ratio of metal salts to bicarbonate. The ratio was slightly shifted towards NH_4HCO_3 (1:3) to ensure the complete formation of mixed metal hydroxide/oxy-hydroxide/carbonate. The dried precursor powder was calcined for two hours at 350 °C and used for further characterization and electrochemical nitrite detection experiments [37]. The resulting spherical nanoparticles with individual sizes of 10 to 30 nm were highly agglomerated as seen by FE-SEM. The high specific surface area ($168.04 \ m^2g^{-1}$), large pore size, and volume revealed the mesoporous nature of spinel $NiFe_2O_4$ nanoparticles suitable for electrochemical nitrile detection.

A distinctive structural, magnetic, and optical properties of potential $BiFeO_3$ photocatalyst additionally stated the value of rapid SD synthesis. The formation of well-crystallized $BiFeO_3$ nanocrystallites started at a temperature of 450 °C. After calcination at 600 °C for one hour, the crystallite size is found to be 31.4 ± 5.0 nm with primary particles measuring around 200 nm. Magnetic analysis of the $BiFeO_3$ samples showed the ordinary behavior of an antiferromagnetic material. The direct optical band gap was calculated to be 1.85 and 2.25 eV based on absorbance and reflectance measurements, respectively [38].

The most complex metal synthesized so far by SD method is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ (BSCF) [28]. Nanocrystalline material was formed after one-hour long heating at 1000 ºC. The evolution of the perovskite phase is followed by XRD from room temperature up to 1000 ºC. The produced BSCF phase was composed of nanocrystals measuring from 20 to 25 nm (XRD analysis data) while agglomerates measured around 300 nm (SEM analysis data). This research witnessed that the SD method offers simple, rapid, and energy-efficient synthesis of complex oxides such as BSCF.

4. FUTURE PERSPECTIVES

In the past years, SD synthesis has become an interesting area of research worldwide because of its advantages and the quality of the materials produced. The traditionally employed physical and chemical synthesis methods usually consume a huge amount of time and energy and are very often harmful to the environment. Additionally, researchers are requiring

oxide materials with nano- and mesoscale pores, crucial for applications in emerging fields such as catalysis, adsorption, sensors, gas purification, as well as in solar cells. Since the first report of the SD method, a lot of research has been carried out, with a variety of oxide nanoparticles developed. However, there is still a need for improvement. Control over the accurate mechanisms for the SD fabrication of nanomaterials is required. The first steps are done in the paper dealing with the synthesis of CeO_2 [39], with much additional work to be done. Almost every oxide material synthesized by the SD method is marked by the unique precursor mechanism and kinetics. The work required is complex but could result in even better control over the size and morphology of the synthesized nanoparticles. Additional efforts must also be made in the direction of SD synthesis implementation at the industrial level.

Further possible application of the SD method is in the field of high entropy oxides [40] - a new class of ceramics known as entropy stabilized oxides or high entropy oxides (HEOs). These multicomponent oxides have created a new opportunity for material design and discovery. The higher entropy materials are a relatively new concept in material science where a large number of elements (by previous standards) are combined in almost equimolar ratios. These materials are called High Entropy Alloys (HEA) and are currently the hot topic of research and investigations. The possibility of stabilizing one single-phase region due to the high entropy of mixing has fascinated the research community as a whole. The first application of HEAs was in structural materials. Due to their exceptional mechanical properties, the HEAs have been investigated since the early 2000s. In recent years, the field has expanded in studies of electronic, ionic, magnetic, and superconducting properties. Quite a few different classes of HEOs have also been investigated and showed promising results [41,42,43]. Now different materials including oxides have been stabilized using high entropy of mixing by numerous elements. The SD method could be used for the synthesis and further modification of these materials.

Finally, precursors heating could be transformed from conventional to microwave. SD method deals with ammonium bicarbonate and metal nitrates sensitive to microwave irradiation which could ensure rapid heating and transformation to more de-

sirable oxide nanomaterials. There is of course the question of process control and adjustment, which should be addressed in future research.

5. CONCLUSIONS

The SD method was originally developed for the synthesis of monometallic oxides and hydroxides. The method is found to be economical, fast, and environmentally friendly, producing valuable nanoparticles. The large surface area and mesoporous nature of products opened the application of produced materials in several emerging scientific fields. After the first report, additional research is done concerning the introduction of several different dopants in the oxides structures. It is confirmed that water scarcity during synthesis adds to the stability of the doped systems. This is found especially important for the catalytic systems. Simple temperature tuning during catalyst synthesis is found to strongly influence the structure-activity relationship.

Other valuable tools for modification of resulting nanoparticles are water rinsing, and reactants (metal nitrate to ammonium bicarbonate) ratio shifting. The rinsing is found to have a positive effect on various nanoparticle characteristics, while the ratio of the reagents influenced nanoparticle size.

There are also notable steps in determining the exact mechanism and kinetics of SD synthesis. Together with known reaction parameters, this should provide full control over the whole process and final material characteristics.

Additionally, the SD method proved to be a powerful tool for mixed metal oxides synthesis. This is found very useful due to these materials' superior characteristics. The resulting improved microstructure is found to be of interest in many materials whose favorable characteristics previously reached a limit.

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ПРЕГЛЕД РАЗВОЈА СИНТЕЗЕ СА НЕДОСТАТКОМ РАСТВАРАЧА

Сажетак: Изазови савременог друштва и захтјеви за високотехнолошким материјалима довели су до нове етапе у развоју метода хемијске синтезе. Ова фаза тражи поуздан, контролисан и еколошки прихватљив приступ производњи неопходних материјала. Једна од недавно развијених техника за синтезу наночестица металних оксида је метода са недостатком растварача. Најважнија предност ове методе синтезе је могућност контроле хемијске трансформације која резултира оптималним условима за производњу материјала. Као резултат тога, оксидне наночестице се производе брзо, еколошки прихватљиво, јефтино, и са малом потрошњом енергије. С друге стране, сложени реакциони механизам представља изазов за поуздане кинетичке студије. Овај преглед прати недавне трендове у развоју методе са недостатком растварача а везано за истраживања бинарних, тернарних и комплексних металних оксида. Посебна пажња посвећена је разматрању синтезе оксида за каталитичке примјене. У будућем развоју, очекује се да ће се наведена метода синтезе користити у припреми високо ентропијских оксида. Због једноставне припреме, такође је могуће аутоматизовати поступак неопходних операција и истражити велики број могућих композиција што је императив за нове сложене материјале. На крају, загријавање прекурсора може се радити у микроталасним пећима. Метода са недостатком растварача користи прекурсоре осетљиве на микроталасно зрачење који би могли осигурати брзо загријавање и трансформацију у пожељне оксидне наноматеријале.

Кључне ријечи: синтеза са недостатком растварача, наночестице, оксиди метала.