How to Cite:
Rajwanti, & Tyagi, D. (2022). Nanosized sulfated zirconia with brnsted acid sites prepared without the use of solvents using zircon-based ZR (OH)4 mediated zirconia 1-D nanomaterials. *International Journal of Health Sciences*, *6*(S3), 8501–8509. https://doi.org/10.53730/ijhs.v6nS3.8008

Nanosized sulfated zirconia with brnsted acid sites prepared without the use of solvents using zircon-based ZR (OH)4 mediated zirconia 1-D nanomaterials

Ms Rajwanti
Research Scholar, Starex University, School of Physical Sciences, Department of Chemistry

Dr. Divya Tyagi
Professor, Starex University, School of Physical Sciences, Department of Chemistry

***Abstract*---**Zirconia 1-D nanomaterials have shown extraordinary and unique capabilities ranging from electronics and medical technologies to chemical engineering and biotechnology. Polyethylene glycol 6000 (PEG6000) was used as a structure-directing template to guide the synthesis of zirconia 1-D nanomaterials from zirconium hydrates manufactured locallyof the nanomaterials. There was a wide range of PEG/Zr mole ratios (0.067 to 0.167), pH was set at 9, the temperature was set at 80°C, and the ageing periods were anywhere from one to three hours. For the mineralogy of the synthetic zirconia, an X-ray diffractogram was employed, and the thermal behaviour of the zirconia was evaluated using a thermal gradient differential thermal analysis technique (TG-DTA). Meanwhile, scanning and transmission electron microscopes were used to study the zirconia that had been manufactured.

***Keywords*---**nanosized sulfated, zirconia, brnsted acid, zircon-based ZR $(OH)_4$, nanomaterials.

Introduction

A growing body of research has focused on material with a one-dimensional nanoscale structure, such as: microneedles (nanowire) microribbon (nanotubes). This is due to the importance of these materials in future technological applications and fundamental scientific study. Because of the vast variety of applications that ZrO_2 might serve as a consequence of its good physical and

chemical features, it has been widely researched. These include resistance to mechanical and thermal stress, low electrical conductivity and biocompatibility are only few of the properties that make a material useful, among other characteristics. A wide range of applications for zinc oxide (ZrO_2) are found in a variety of products such as Electrochemical devices (capacitors), membrane reactors, microelectronic devices, and protective coatings are all examples of transparent optical components. Other uses for zinc oxide (ZrO_2) include oxygen sensors, magnetic materials, heterogeneous catalysts, and electrolytes in solid-oxide fuel cells. Other environmental applications that ZrO_2 may be employed in include the catalytic filtration of harmful gases and the manufacture of biodiesel, among others. The use of ZrO_2 is greatly impacted by the form and structure of the material. Because of their large specific surface area5, zirconia nanoparticles have a higher catalytic activity than other nanoparticles. Despite the fact that it is difficult to separate nanosized particles from reaction medium, it is possible that a significant amount of nanosized particles is lost during the recycling process. Nanocatalysts made of ZrO_2 on the other hand need more investigation. Analytical oxidation was recently used in the production of ZrO_2 nanotubes.

Production of ZrO_2 Nanopowder, thin films, nanotubes, nanorods, nanobelts, nanowires, and nanoneedles are all examples of nanocrystalline materials. may be accomplished by a variety of technological approaches. Zirconia nanotubes have been produced using a variety of techniques, including template-assisted deposition, hydrothermal treatment, and anodic oxidation processes. Cao et al. employed template methods to synthesise optically useful tetragonal zirconia nanowires, which they found to be beneficial in a variety of applications. The surface morphology and crystallinity of thin-film zirconia are critical for some applications requiring fine control over these properties. Because of the large surface area and high porosity required for film humidity sensors, their sensitivity to changes in humidity may be increased by using larger sensors. PVD, sputtering, CVD, plasma spraying, electron-beam deposition, and a range of other procedures are used to produce zirconia thin layers on a variety of substrates.

These techniques are time-consuming and expensive, and they make it difficult to create very porous layers. Ksapabutr et al. employed zirconatrane as a precursor in the electrostatic spray deposition of zirconium dioxide nanostructures on a glass substrate, and they found that it was effective. During their investigation, they discovered that zirconia structures had nanoneedle and nanoflower morphologies. Thin layers of ZrO_2 were used to create sensors that were evaluated for their capacity to detect humidity. Humidity sensors made of zirconia in the form of flowers were shown to be more sensitive, recover quicker, and be more dependable than needle-shaped sensors. ZrO_2 nanorods were synthesised by the use of an inverse microemulsion process that was previously disclosed by Liu et al. For the successive syntheses and conversions of zirconium nanograins anodizing, and annealing in argon ambient gas were used to create zirconia nanoneedleshas yet to be examined.

For zirconia, plasma spraying is the preferred commercial coating processbecause of its high durability. Multiple disadvantages of plasma spraying have been identified, including the difficulties to create excellent adhesion between the coating and the substrate, the presence of several undesired phases, and the poor

cohesiveness of the coating. Because of this, other processes including as sol-gel, anodic oxidation, PVD, and CVD have all been investigated as viable replacements to plasma spraying. In the case of thin oxide Zr, Ti, Si, P, and Ca films, PVD is a technique that may be applied. Purified zirconium nanograins (Zr) will be utilised to make ZrO_2 nanoneedles, which will be produced utilising uncomplicated processes in which every product employed at There is a specific purpose for each phase in the process (e.g., biomedical applications, sensors, capacitors, magnetic materials, and energy).

Zirconium nanograins were deposited on a silicon substrate using PVD magnetron sputtering. Anodizing the zinc-coated substrates allowed for the fabrication of ZrO_2 nanotube arrays. It was decided to employ an argon gas environment to anneal sample coated with a thin layer of ZrO_2 and heated at various temperatures (e.g., 450, 650, 855, 905, and 950 °C) in order to see what happened. A total of two methods were employed in this study: X-ray diffraction and scanning electron microscopy with field emission (FESEM). Surfaces were evaluated for their ability to promote cell adhesion, growth, and proliferation, among other things. In a nutshell, heating the ZrO_2 resulted in a significant improvement in its biocompatibility.

Catalyst development in the 'nano-scale' model of sulfated zirconia

Biolubricants, which are non-toxic and biodegradable, provide a number of advantages over traditional lubrication materials. You won't have to worry about anti-oxidants, index-improving agents, stabilisers, or detergents since they'll take care of everything. Because their viscosity does not fluctuate with temperature, they can lubricate across a wider temperature range than conventional lubricants. The majority of the fundamental components used in biodegradable lubricants are obtained from plant sources. Synthetic biolubricants may be produced by esterifying free fatty acids (FFAs) derived from vegetable oils with alcohols in the presence of catalysts, which is similar to the process used to manufacture natural biolubricants. In the catalysis of esterification processes, acid-based homogeneous or heterogeneous catalysts, especially sulphuric or phosphoric acids, are often utilised as catalysts. Heterogeneous catalysts have the potential to overcome many of the problems associated with homogeneous catalysts, including vessel corrosion and catalyst separation. A number of solid acid catalysts for the synthesis of vegetable oil esters have been identified and reported before in the literature. The esterification reaction of FFAs and methanol was carried out with the help of a heterogeneous catalyst, sulfated zirconia. This resulted in the production of biolubricants. The crystallographic phase of zirconia has a major influence on the surface acidity of zirconia (SZ). When sulfated, tetragonal zirconia has a larger surface acidity and catalytic activity than monoclinic zirconia, which has a more stable structure and has a lower surface acidity. The initial activity of heterogeneous FFA esterification catalysts is determined by the acidity of their surfaces.

The SZ system's ability to maintain high FFA esterification selectivity even in the presence of large amounts of alcohol is a major advantage. When a large amount of alcohol is utilised in the FFA esterification process, it increases the likelihood of dehydration and other undesirable consequences as a result (to form dimeric

ether). As a catalyst for reactive distillation-aided FFA esterification at high alcohol/acid ratios, SZ shows minimal activity for dehydration and excellent selectivity in the presence of excess alcohol. The activity and durability of SZ can be increased by combining it with other metal oxides in the production of mixed oxides. It has been demonstrated that a homogeneous combination of oxides (MoO_3–Nd_2O_3, MoO_3–Nd_2O_3) that stabilises the tetragonal ZrO_2 phase and increases the esterification activity and sulfurleaching resistance of SO_4^{2-}/ZrO_2 significantly increases the esterification activity and sulfurleaching resistance.

Nanosized sulfurated zirconium with attached acidic sites is completely solvent-free

Zirconia has recently attracted a lot of attention for its potential as a catalyst or catalyst support. Zirconia has a very small surface area in general. To increase the surface area of zirconia, a number of ways have been used, including the development of nanocrystalline, mesostructured, and meso-macroporous zirconia, among others. Sulfated zirconia may prove to be a beneficial addition to the zirconia family for industrial processes such as hydrocarbon isomerization, alkylation, and esterification, among others. It is not possible to utilise sulfated zirconia in significant quantities in catalytic processes due to the material's low surface area. Since ancient times, people have been fascinated by the huge surface area that sulfated zirconia has. Preparations of sulfated zirconia that have a wide surface area have been shown to be beneficial in a variety of circumstances. There are many different types of sulfated zirconia that have been described in the scientific literature.

Some of these types include mesoporous zirconia that was synthesised from surfactants, sulfated zirconia nanopatches that were prepared by reverse microemulsion and sol-gel techniques, and monoclinic and tetragonal sulfated zirconia with high surface area that was prepared by one-step crystallisation.... In the creation of these goods, the use of solvents is another component that contributes to the complexity of the situation. The acidity of sulfated zirconia catalysts may be affected by a number of different factors, such as the production technique, the zirconia crystalline phase, the calcination temperature, the species of sulphur, and the catalyst surface area. The texture of the final product and the performance characteristics of the sulfated zirconia catalyst at hand are both significantly influenced by the catalyst's precursor. The amorphous form of $Zr(OH)_4$ is the ideal precursor for the sulfation reaction to take place. Due to the impossibility of the process, zirconium oxide cannot be sulfated in order to generate a high degree of acidity. The temperature at which a catalyst is calcined may have a significant impact on the amount of catalytic activity it has. In order to sulphate zirconia, the material is typically subjected to temperatures ranging from 550 to 650 degrees Celsius throughout the process.

As a consequence of the many experiments that were conducted on the active sites of this material, it is now common knowledge that sulfated zirconia has both Brnsted and Lewis acidic sites. The presence of strong acid sites in sulfated zirconia has been attributed variously to Lewis, Brnsted, or a mixture of the two acidic sites; nevertheless, the exact cause of these sites is still up for debate. According to the widely recognised hypothesis of n-butane isomeration, the

dehydrogenation of n-butane results in the formation of n-butene. There have been a number of various approaches developed by researchers to produce n-butene, including the use of Brnsted acidic sites, Lewis acidic sites, or a combination of the two on sulfated zirconia. Without the use of a solvent, sulfated zirconia nanoparticles with huge surface areas (165-193 m2/g) may be produced by heating $ZrOCl_28H_2O$ and $(NH_4)_2SO_4$ to 600°C for an extended period of time. The infrared spectra of adsorbed pyridine clearly demonstrates that the Brnsted acidic sites in nanosized sulfated zirconia are more frequent than in bulk sulfated zirconia. Catalytic investigations on the As an example of a reaction catalysed by Brnsted acidic sites, researchers have shown that nanosized sulfated zirconia exhibits more activity in the esterification process than normal sulfated zirconia.

Zinc 1-D nanomaterials from zinc-based ZR(OH)4 mediated by peg-6000. zirconia 1-d nanomaterials

The research of one-dimensional (1-D) nanomaterials has increased in recent years, owing to its outstanding properties, which include dense, very porous material that has excellent strength-to-weight ratios, among others. Using a 1-D nanomaterial such as zirconia (ZrO_2) as an example, sensors, catalysts, biomaterial composites, and other applications in a number of industries, including electrical, chemical, and pharmaceutical, are possible. Sol-gel, deposition method, and chemical route have all been used to create ZrO_2 1-D nanomaterials, as have anodization, hard-template approach, and electrospinning. Other methods used to create ZrO_2 1-D nanomaterials have included electrospinning. Precursors for zirconium in those techniques were mostly made up of organometallic compounds, salts, and Zr metal, which were all used extensively.

ZrO_2 1-D nanomaterials were synthesised using a straightforward approach that included PEG-6000 and a cheap precursor of zircon-based Zr $(OH)_4$ from a nearby zircon source. As a one-dimensional template for the organic polymer PEG6000, it was also used in this experiment. In the synthesis, an ageing treatment was mixed with ultrasonic therapy to provide a more youthful appearance. Ultimately, it was hoped that the treatment would minimise particle contact to a minimum, resulting in less agglomeration. In previous work, we demonstrated that an ultrasonic ageing process supported by organic polymers such as PEG4 and starch may be used to successfully create a 1-D Al_2O_3 nanomaterial. The researchers observed that ultrasonic ageing may be used to analyse the effects of the ageing method, temperature, and composition ratio on the characteristics of nanomaterials as a result of their study, which they published in Nano Letters. It was discovered that ultrasonic irradiation may be utilised to treat the manufacture of 1-D Al_2O_3 nanomaterial, which led in the synthesis of nanofibers and rods with lengths ranging from a few hundred nanometers to several thousand.

It was discovered that the synthesis of these ZrO_2 1-D nanomaterials was possible from a local zircon-based $Zr(OH)_4$ precursor by utilising PEG6000 at various PEG-6000/Zr ratios and ultrasonic treatment throughout a range of ageing periods in this study effort. To produce the $Zr(OH)_4$ precursor, which has the formula $Zr(OH)_4•xH_2O1_5$ in our previous work, we used a modified sodium carbonate

sintering technique that was adapted from the standard procedure. As a result, ZrO_2 does not develop a 1-D microstructure as a result of the presence of hydrate molecules in the precursor. This is because the (OH) groups of the precursor and the (O) groups of PEG-6000 are not able to establish hydrogen bonds. Therefore, it is anticipated that ultrasonic treatment will allow the precursor and PEG6000 to establish a hydrogen bond during the formation of ZrO_2 1-D nanomaterials, resulting in the dissipation of $Zr(OH)_4$ hydrates throughout the manufacturing process. We have synthesised PEG was used as a 1-D structure-directing template for the formation of 1-D ZrO_2 nanomaterials by ultrasound treatment of local zircon-based $Zr(OH)_4 \bullet xH_2O$; we investigated $ZrO^{2'}$s thermal behaviour and phase transformation, as well as its infrared spectra as it was synthesised; we also observed the impact of ZrO_2's PEG/Zr ratios and ageing periods on its microstructures.

Ultrasonic sound on the structure of amorphous zirconium gels using combined sans and saxs methods

It is possible to synthesise advanced inorganic materials, such as metal oxides and hydroxides, by using the sonochemical approach, which is extensively used in hydrothermal and solid-phase settings, as well as in liquid-phase environments. The ultrasonic-assisted sol–gel technique decreases the amount of time needed for the production of nanomaterials because of the faster hydrolysis. As a consequence, the particle size distribution is more uniform, the surface area is higher, the thermal stability is increased, and the phase purity is improved. Ultrasound-assisted sol–gel synthesis of metal oxides such as ZrO_2 and SiO2 has been used to successfully synthesise nanostructures such as TiO_2, ZnO, and $ZnMo_3$ as well as other materials. Many different types of molecules have been shown to have better qualities over those synthesised using standard processes, and this has been shown in a range of situations. For example, ultrasonic-assisted nickel hydroxides demonstrated superior electrochemical performance than their conventional counterparts. Layered double hydroxides generated utilising ultrasound-enhanced methods were shown to be more easily adsorbable in the presence of humic chemicals. The use of ultrasound has recently been shown for the production of porous adsorbents with a high specific surface area.

The absorption of acoustic energy from power ultrasonography in liquid media results in turbulent fluid movement around cavitational bubbles, which results in a range of physical events in the surrounding medium. When a phase boundary is approached, Microjets and shockwaves are generated at high speeds in this area. Sonic treatment of suspensions containing relatively big particles (d > 0.5–1 m) may result in amorphization and other consequences, such as deagglomeration, a drop in mean particle size, an increase in surface area, and others. At the solid-liquid interface, researchers have uncovered some intriguing relationships between the wettability of a surface and the nucleation and burst of cavitation bubbles. It is crucial for the industrial sector to employ zirconia and zirconia-based products because of their vast range of uses (catalysts, oxygen-conducting materials etc.) When making these materials, the easiest method is to start with precursors rich in zinc, such as zirconyl nitrate or zinc alkoxide, and then heat or hydrothermally treat the $_{ZrO2xH2O}$ gel. There are several factors that determine how synthesised zirconia is formed, including the gel structure and precipitation

temperature of the precursor gel, as well as the circumstances under which it is formed (e.g. composition, temperature, acidity of starting solution, etc.) The relative rates of zirconium-based cluster hydrolysis and condensation, for example, are affected by variations in precipitation pH. The creation of a metal oxy-hydroxide network occurs when there is an excess of alkali in the reaction media, resulting in fast hydrolysis and condensation. With zero charge, the surface area of hydrous zirconia precipitated at zero charge is greater than that of hydrous zirconia precipitated at a low pH. It was found that gels made from zirconium isopropylate exhibited comparable behaviours. Amorphous hydrous zirconia made by the sol-gel method may keep its high surface fractal dimensions following crystallisation.

Ultrasound has recently been utilised to synthesise zirconia-based materials, which has caught the interest of those who are interested in this field. It has been shown that ultrasonic cavitation may disaggregate zirconia colloidal particle agglomerates, reduce the amount of physically and chemically bound water (as well as the number of adsorbed ions), and dramatically increase the specific surface area of zirconia amorphous samples. The use of ultrasonic waves to treat zirconia resulted in a more rapid transition from the monoclinic to the tetragonal phases. Despite the fact that ultrasonication has a direct impact on the structure of amorphous hydrous zirconia formed during sonochemical-aided precipitation, the structural features of this material are still relatively unstudied. The relevant scientific reports are also inconsistent with one another. In the case of ZrO_2 particles, sonication has been shown to drastically lower the gyration radius of the particles and to accelerate the formation of linear polymeric clusters. However, our subsequent studies using sonochemically generated amorphous zirconia gels revealed an increase in the surface fractal dimension as well as the size of individual particles, in contradiction to the previous results. Until far, the majority of the research on the fractal structure of gels generated by ultrasound has been conducted on hydrous silica gels. According to Vollet et al., ultrasound-stimulated silica gels, for example, have a lower fractal dimension than typical silica gels because they are less elastic. When both materials were dried, it was discovered that the former had higher pore volumes and specific surface areas than the latter.

Levulinic acid esterification by sulfated zirconia nanoparticles

The current rise in interest in lignocellulosic biomass may be attributed to the fact that it has the potential to serve as a source of valuable chemicals and liquid fuels. Since LA originates from lignocellulosic biomass and may be converted into fuel additives, polymers, and speciality chemicals, it is a platform molecule that is appealing for use in a range of chemical applications. It is possible to produce diphenolic acid from levulinate esters, valerolactone, 1,4-pentanediol, and 5-nonanone. Diphenolic acid serves as an intermediate in the synthesis of epoxy resins and polycarbonates (through pentanoic acid). Levulinate esters have the potential to improve the performance of fuel additives, solvents, and plasticizers. As a possible consequence of this, the use of fossil fuels derived from petroleum might decrease. This is really encouraging news for the environment. When LA is esterified with alcohols and mineral acids such as HCl, H_2SO_4, and H_3PO_4, this process ultimately results in the production of levulinate esters.

Utilizing mineral acids may have a number of unintended consequences, including toxicity, corrosion, and difficulty in recovery. As a result of this, it is of the utmost importance to discover homologous analogues of heterogeneous catalysts that are capable of being cleaned up and used again. In order to carry out esterification operations, scientists have made use of a wide range of materials, such as zeolites, Wells-Dawson heteropolyacids, and sulfated oxides. Altering the dispersion state and acid site count of sulfated oxides as they are being prepared may lead to increased activity. This can be done.

Alterations might be made to the conditions of the preparation in order to accomplish this objective. Micelle templating might be used to incorporate mesopores into metal oxides in order to boost acid site dispersion. This would be accomplished by combining the two materials. Improved acid catalytic stability was seen in sulfated ZrO_2 catalysts with greater Si/Zr ratios (up to 30 mol percent Si/Zr). The method of preparation that is utilised to create sulphated zirconia is highly crucial to the manufacturing process of this material. The conditions of its formation and the sulfation process that is used to produce it are the primary factors that determine its physicochemical features. According to what Parvulescu and his colleagues discovered, sulfated zirconia catalysts $(OH)_4$ may be manufactured using a colloidal sol-gel process with peptizing agents such as H2SO4 or CH3COOH. Arata et al. used zirconium sulphate as a Zr precursor, despite the fact that the amount of sulphate that was present in the zirconium sulphate could not be controlled. Tichit et alsol-gel .'s synthesis of sulfated zirconia catalysts called for the use of sulfuric acid to hydrolyze a solution of zirconium alkoxide in n-propanol. This was accomplished by adding the acid to the solution. Using zirconium alkoxide precursors and the sol-gel process, Ward and Ko created what they referred to as the "one-step approach" for the production of zirconia alkoxide aerogels."

Conclusions

To show for the first time how sonication affects the structure of amorphous hydrous zirconia gels formed at various pH levels, we used three complementary methods of characterisation of porous materials on nanometer length scales. These methods are low temperature nitrogen adsorption, small-angle neutron scattering, and small X-ray scattering. ZrO_2-xH2O precipitated from zirconium n-propoxide under ultrasonic processing showed more structured surfaces (surface fractal dimension 2.9–3.0) and a greater specific surface area (approximately 240 m2 /g, instead of the previously reported 220–240). This was in comparison to the non-US-assisted synthesis, which showed a surface fractal dimension of 2.9–3.0. Previous research has shown that subjecting amorphous hydrous metal oxide gels to ultrasonication results in a change in the gel's mesostucture. Using an ultrasonic ageing approach, we were able to synthesise zirconia 1-D nanomaterials from $Zr(OH)_4 \bullet xH_2O$ mediated by PEG-6000 at varying concentrations. This allowed us to produce zirconia nanomaterials in one dimension. The researchers found that the temperature required for ZrO_2 to form crystals was around 810 degrees Celsius. This is the case in spite of the fact that ZrO2 1-D nanomaterials were manufactured using a prescribed PEG/Zr mole ratio of 0.167, a pH of 9, a synthesis temperature of 80°C for 2 hours, and a calcination temperature of 900°C.

References

1. Panda P.K., Ceramic nanofibers by electrospinning technique – a Review, Trans. Ind. Ceram. Soc., 66(2), 65-76 (2007)
2. Xu X., Guo G. and Fan Y., Fabrication and characterization of dense zirconia and zirconia silica ceramic nanofibers, J. Nanosci. Nanotechnol., 10(9), 5672-5679 (2010)
3. Jirsak O., Nanofibers, technology and applications, http://www.fzu.cz/~nanoteam/events/ws2006/jirsak, accessed on 27 August (2013)
4. Maryani E., Subagjo Nuruddin A., Septawendar R. and Purwasasmita B.S., Effects of aging and temperature parameters, polyethylene glycol (PEG)/Al ratios on the structure directing mechanism of γ-alumina nanofiber-based Indonesian natural kaolin by ultrasonic aging process, Journal of The Australian Ceramic Society, 51(2), 116 – 122 (2015)
5. Guo G., Fan Y., Zhang J.F., Hagan J.L. and Xu X., Novel dental composites reinforced with zirconia–silica ceramic nanofibers, Dental Materials, 28, 360-368 (2012)
6. Wang J., Jin E.M., Park J.Y., Wang W.L., Zhao X.G. and Gu H.B., Increases in solar conversion efficiencies of the ZrO2 nanofiber-doped TiO2 photoelectrode for dye-sensitized solar cells, Nanoscale Research Letters, 7, 1-4 (2012)
7. H.X. Xu, B.W. Zeiger, K.S. Suslick, Sonochemical synthesis of nanomaterials, Chem. Soc. Rev. 42 (2013) 2555–2567.
8. J.H. Bang, K.S. Suslick, Applications of Ultrasound to the Synthesis of Nanostructured Materials, Adv. Mater. 22 (2010) 1039–1059.
9. P.E. Meskin, V.K. Ivanov, A.E. Barantchikov, B.R. Churagulov, Yu.D. Tretyakov, Ultrasonically assisted hydrothermal synthesis of nanocrystalline ZrO2, TiO2, NiFe2O4 and Ni0.5Zn0.5Fe2O4 powders, Ultrasonics Sonochem. 13 (2006) 47–53.
10. A.Ye. Baranchikov, V.K. Ivanov, Yu.D. Tretyakov, Sonochemical synthesis of inorganic materials, Russ. Chem. Rev. 76 (2007) 133–151.