International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

A Brief Review on Pervoskite Oxides Synthesis and Applications

Shilpa Sangle

MVP Samaj's SSSM Arts, Science and Commerce College, Saikheda (affiliated to S. P. Pune University), Nashik, Maharashtra, India
shilpasangle620[at]gmail.com

Abstract: ***In Recent years, perovskites have been rediscovered as a family of catalysts due to great diversity in many scientific disciplines. Because of the wide range of ions and valences which this simple structure can accommodate, the perovskites lend themselves to chemical tailoring. Research has been focused on synthesizing porous perovskite materials so that large surface areas can be obtained with improved surface properties. It is relatively simple to synthesize perovskites because of the flexibility of the structure to diverse chemistry. Many of the techniques of ceramic powder preparation are applicable to perovskite catalysts. In their own right, they are therefore of interest as a model system for the correlation of solid-state parameters and catalytic mechanisms. Such correlations have recently been found between the rate and selectivity of oxidation-reduction reactions and the thermodynamic and electronic parameters of the solid. Perovskite-type materials have become a research hotspot in the field of materials science due to their excellent structural stability and physicochemical properties. It has numerous potential applications including heterogeneous catalysis, photocatalysis, as gas sensors and in batteries. This paper briefly reviews the preparation methods of perovskite materials and their use as catalysts.***

Keywords: perovskites, synthesis, applications

1. Introduction

Catalysis is the process in which the chemical reaction rate is increased with a catalyst [1]. Catalyst is required in very small amount because in the reaction it is not consumed and reused several time [2]. As compare to non-catalysed reaction, catalysed reaction gives an alternative pathway with lower activation energy, so chemical reactions occur faster. Catalyst reacts to form a temporary intermediate, which then regenerates the original catalyst in a cyclic process. The reaction rate decreases due to the non-catalysed route [3] and not due to mechanism with higher activation energy.

Catalysts are classified into two types 1) homogeneous 2) heterogeneous catalyst. A homogeneous catalyst and the reactant molecules are in the same phase. A heterogeneous catalyst and the reactant molecule are in the different phase. Third category of catalyst is enzymes and other biocatalysts. The industrial production of most important chemicals and biochemically significant processes are based on heterogeneous catalysis. In applied science, organometallic chemistry and materials science involves major field of research in catalysis. Reactions carried out by using catalyst are eco-friendly due to non-toxicity, less waste generation properties [4]. Many transition metals, transition metal complexes, metal carbonates and perovskite metal oxides are used in catalysis.

One of the most important and widely characterized heterogeneous catalysts which are used for and redox acid base reactions are metal oxides. Transition metals, paid the attention due to their outer electron configuration. They are used as catalyst in different reactions such as oxidation, dehydration, dehydrogenation, and isomerization. The transition metals oxides such as Nb_2O_5, WO_3 [5], and TiO_2 [6] are widely used as heterogeneous acid catalysts [7]. In many areas of chemistry, a metal oxide plays an important role especially in material science [4-7]. Therefore metal oxide nanomaterial are widely studied by the researchers. Metal oxides are modified either by doping or coating of metal or by forming composite with other metal oxide.

Over recent decades, many new composites of pervoskite type of oxides have been developed, some with very valuable properties [8]. From last few years, the use of perovskite type compound as catalyst has been investigated. Perovskite oxide nano crystals show important properties like ferroelectricity, piezoelectricity, dielectricity, ferromagnetism, and multiferroics. Various properties of pervoskite oxides are connected to the framework of BO_6octahydra [8] and the state of B-site cations [9, 10], but brownmillerite ($A_2B_2O_5$), shows A is large s, d or f block cation and B is transition metal cation, is an oxygen deficient type of perovskite with three dimensional framework of corner connecting BO_6octahydra which are obtained due to lack of oxygen during the formation of the structure [11, 12]. Perovskite and brownmillerite have been widely studied [13, 14]. Almost every element on the periodic table, apart from the noble gases, has been incorporated into the perovskite structure.

Perovskite oxides are studied and applied in a large scale because they shows a variety of solid-state phenomena from, semiconducting, metallic, insulating, superconducting characters and electrical properties. Due to good physical and chemical properties perovskite type oxides shows many practical applications and have been given high catalytic activity for carbon monoxide, methane, propane, hexane and toluene oxidation. Thus, it can be used in combustion automobile exhaust, and waste gas purification as a catalyst. Apart from this, it can be used as an electrode material for solid-electrode fuel cells and gas sensors.

2. Synthesis of Perovskites

The conventional synthetic method employed in solid-state chemistry is called ceramic methods, which involves mixing and heating at elevated temperature of readily available reactants. The choice and activity of catalyst is mainly depends on way of preparation, heating and there by preparation of catalyst is a crucial factor. The well-known methods used for the synthesis of perovskite metal oxides and modified metal oxides are explained below.

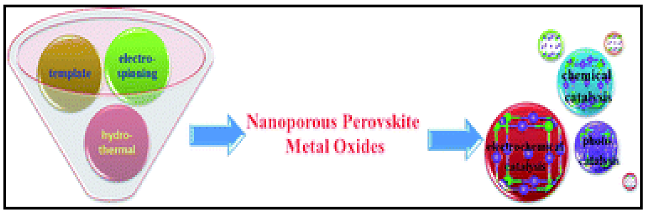

Figure 1: Methods of preparation of Perovskite metal oxides

2.1 Solid-State Reaction Method:

It is the regular process for the preparation of perovskite metal oxide nanocrystals [16, 17]. This method involved mixing, milling, and calcining starting materials at desired temperatures to get the perovskite metal oxide. The high-temperature heating gives an agglomerated powder that requires further milling process which can create defects in the manufactured products. Recently $BaTiO_3$ nanocrystals are synthesized by Buscaglia et al. at 800°C [18].

2.2 Co-precipitation method:

Precipitation is sole conventional method by which sparingly soluble products from aqueous solutions are further decomposed to yield oxides. The co-precipitation process involves dissolving salt generally chloride, nitrate or oxychloride, including $AlCl_3$ to prepare Al_2O_3, Y $(NO_3)_3$ to synthesize Y_2O_3, and $ZrOCl_2$ to obtain ZrO_2. When salts are dissolved in water in presence of basic solution i. e. sodium hydroxide or ammonia solution in which metal hydroxides are precipitate out. The resulting precipitate washed and filtered to remove free salts and the hydroxide to obtain the final oxide powder.

In this method difficulties encountered for desired particle size and morphology which can be achieved by using various types of surfactants, sonochemical methods, and high-gravity reactive precipitation [21-23]. Amorphous material is obtained when co-precipitation method is applied at room temperature. When hydroxides, carbonates and oxides of metal combine to obtain single phase mixed metal oxide which is heated to obtain co-precipitation. It is difficult to assign experimentally, whether it is single or multi-phase.

2.3 Sol-gel method:

In this technique metal oxides are obtained by hydrolysis of starting materials, in alcoholic solution, which gives hydroxides. When molecules are condensed it forms a network of the metal hydroxide which undergoes polymerization. Proper drying and heating of porous gel lead to ultrafine porous oxides [24].

Various metal oxides and mixed metal oxides with different forms, i. e. powders, coatings, thin films, fibers, monoliths and porous membranes. The advantages of the sol-gel technique is better homogeneity, more purity, low synthesis temperature, better size and morphological control, as compared with the traditional ceramic method. It can produce amorphous materials, easy preparation of thin films, coatings, glasses and ceramic with better homogeneity and purity as compared to high temperature conventional methods. Hence the sol-gel method is widely applied in ceramic technology.

2.4 Micro-emulsion technique

This technique is commonly used for preparation of nanoparticles which are produced in the cavities. It contains mixture of water, a surfactant and oil shows an approach depend on the formation of micro/nano-reaction vessels. Metal precursors undergo precipitation within the aqueous droplets as oxo-hydroxides, which leads to mono-dispersed materials **[25].** The droplet sizes are generally higher than 100 nm up to even few millimeters. The significance of this method is the bio-degrability and biocompatibility of prepared materials. Bio-degrability reduce environmental pollution and biocompatibility gives unique applications in drug delivery.

2.5 Solvo-thermal method

In solvo-thermal techniques, decomposition of metal complexes takes thermically using an autoclave using pressure or boiling in an inert atmosphere. In order to control growth of particle and control agglomeration a specific surfactant agent including long chain amine, thiol, trioctylphosphine oxide (TOPO) is usu2ally allowed to react with media. The stabilizers also help in dissolution of the particles in different solvents.

This method has more advantages due to increased solubility and reactivity of metal salts with increased temperatures and pressures without reaching the solvent at its critical point. In solvothermal process temperatures required is less as compared to other technique.

2.6 Template/Surface derivatized method

Such methods are commonly used to synthesis varieties of porous materials. Surface-and template-mediated nanoparticles precursors have been applied to prepare self-assembly systems [21**].** To obtain various HSMO and mono dispersed oxides commercial active carbons are used as template. However, it has few insignificance during high temperature because in synthesis carbon may react with each other and destroy the material. The carbon present may get oxidized at lower temperature if heat treatment is performed in air. On the other hand, it is well known that carbon is better reducing agent at high temperature with inert atmosphere, so metal salts are reduced and it may give metal rather than metal oxide.

2.7 Spray pyrolysis

This is a Chemical Vapor Deposition technique which is used for preparation of thin and thick films. This method is simple, easier, and simple apparatus to prepare thin film of different constituents. It produces the droplets of aerosol from starting sol, suspension or solution by nebulization or atomization method. Evaporation of obtained droplets takes place and condensation within the droplet and is dried by thermolysis process.

This technique has number of other names, such as solution aerosol, plasma vaporization, thermolysis, evaporative solution decomposition and decomposition of aerosol. It is useful method for the synthesis of highly pure homogeneous oxide powders. The precursors used in this procedure are generally proper salts in solution, suspension or sol form. Different processes are used for the conversion of the aerosol droplets into particles such as thermolysis of precipitated particles. Generally aqueous solutions are applied due to their lower cost and presence of water soluble salts [41-45].

One advantage to this process is including the recovery of highly pure nanoparticles and their homogeneity, no subsequent milling is necessary and it is one step process. The voluminous amount of solvent is required and the difficulty of scaling up the production is the disadvantages of spray pyrolysis method.

2.8 Microwave method

Microwave assisted method is used for the preparation of ceramic oxides, hydroxide, porous materials, and hematite material [**26**-**29]. **This technique imposes many significance over regular synthesis methods, including cheaper procedure, fast self-heating and preparation of new kind of materials.

The microwave method for preparation of nanoparticles involves fast heating of the reaction mixture. Because of this, the occurance of nano particles is fast and instantaneous, giving fine particle size with narrow pore size distribution in the particles. This method requires minimum reaction time and hence it is used for the preparation nanoparticles like Ag, Au etc and many metal oxides such as Fe_2O_3, NiO, ZnO, CuO **[**46, 47] etc. This is one of the good method for the synthesis of mixed metal oxides.

2.9 Sono-chemical co-precipitation

Now days, ultrasound irradiation is widely applied for the synthesis of valuable metal oxides with unusual properties. It gives the formation of much smaller particle size with higher surface area. Method involved a high intensity ultrasonic probe dropped directly in the solutions which cause the precipitation of metal, under ambient air for a definite time interval with change in pulse of the order of one or two seconds.

The principle of this technique is based on the chemical bond by using high intensity ultrasound waves, generally between 10 and 20 MHz. Acoustic cavitation is the physical phenomenon which is cause for the sono-chemical method. Reports in literature reveals that for the formation of nanoparticles by sono-chemistry, the important step takes place during the growth and collapse of the nano regime size range solvent bubbles are. generated in the liquid. Then vapor of solute enters into the solvent bubble then the bubble reaches a certain size, it collapse. High cooling rate is required because in few nanosecond bubbles are collapses which affects the organization and crystallization of the products. Amorphous nanoparticles are formed when bond breaks in the precursor but couldn't understand the formation of nanostructure. The formation of nanostructure is due to formation of few nucleation centers in each collapsing bubble and growth of nuclei does not stop and the growth is limited by the collapse.

2.10 Mechanochemical method

Mechanochemical synthesis has gained much interest in industrially important complex composition oxides and for processing ceramic powders. The study of the mechanisms and kinetics of mechanochemical reactions is one of the most important research areas, which form the basis of the further development of mechanochemical synthesis.

In general, complex ceramic oxides exhibit a wide range of properties, which shows attractive range of different applications. Eco-friendly preparation of final product directly during milling and the mechanochemical energetic synthesis with respect to high-energy milling, used to change the reactivity of product, which is followed by an annealing step to obtain the recovered product of complex oxides with a variety of properties. From literature data available it is observed that the influence of mechanochemical activation on both the phase formation during subsequent annealing and the preparation of the final ceramics, the influence of milling conditions, such as humidity, and the effect of the hydration state of the reagents on the course of the mechanochemical reaction as well as the issue of contamination during milling.

This method effects a chemical reaction by using high energy mechanical milling. These methods consist of various processes, such as milling of the type of ball, colloidal, jet and hand grinding. Performing this methods energy is given to the reactants and produces lot of changes including friction, deformation, fracture, quenching and so on. Reactant interfaces shows that, new product phase is generated which grows further with transfer of atoms of the reactant phase, which possess a barrier layer preventing further reaction and the chemical reaction realized [51**].** It has been widely applied in the synthesis of ceramics, ferrites, oxides inorganic and organic preparation, metallurgy, construction materials, activation of catalysts, and pharmaceutical industry [52].

Mechanochemical synthesis is precise for obtaining nanosized material particles with a uniform distribution of grain sizes. The prime significance of this technique is its suitability for large scale production as well as its simplicity in the synthetic process and lower cost.

3. Applications of Perovskite

3.1 Inorganic functional materials

In recent years, due to interesting optical and electrical properties nano-structural inorganic materials has studied, and used in optics, electronics, and sensors as building blocks in bottom-up assembly [69-62].

3.2 Magnetic material

Magnetic nano-sized oxides can be used in catalysis and biomedicine due to their fascinating properties. These materials are also used in magneto caloric refrigeration systems, spin-valves, spin-transistors, and ferro-fluid technology [63-64]. $LnFeO_3$ (Ln=lanthanides) technologically applied as magnetic material [65, 66].

3.3 Coating on automobile windows

Different types of oxide coating films such as UV absorbing coatings, reflective coatings, water repellent coatings, and colored coatings are used to avoid adverse effect on living organisms due to the harmful radiation coming from sun [67, 68].

3.4 Photovoltaic

In commercial photovoltaic inexpensive base materials used is the synthetic perovskites oxides for high-efficiency [35, 36]. Conversion efficiency observed was up to 22.1% [36, 37] and can be prepared by same technique used for preparation of thin film silicon solar cells [38]. Due to high photoluminescence quantum efficiency of perovskites, they are also used in light emitting diodes (LEDs) [40]. Laser emission was observed in perovskite $LaAlO_3$ doped with neodymium at 1080 nm [39].

3.5 Gas sensors

Sensor can detect any change in temperature, pressure, humidity or any gas or liquid molecule at its ambient atmosphere. Since 1962 it has been known that metal oxide shows variation in the conductivity because of adsorption or desorption of a gas on the surface of a metal oxide which is first demonstrated using ZnO thin film layers [30]. Gas sensor is one of the significant application of metal oxides and mixed metal oxides, which can be used for low cost detection of combustible and toxic gases. Gas sensing device has been developed due to the need of detection of toxic and flammable gases. It is necessary to develop reliable and selective solid-state gas sensors because it has many industrial applications but important one is the environment monitoring. Numerous metal oxides have been reported as gas sensors, including perovskite oxides [**69-70].**

3.6 Fuel cells

In future electricity can be generated by using fuel cells. In solid oxide fuel-cells (SOFC) mixed metal oxide nano-materials is used as electrode. Perovskite-type $LaCoO_3$ are promising materials for the SOFC cathode [38-42]. SOFCs are highly effective systems (50 to 65%) for production of electrical energy and it is environmentally acceptable. In high temperature fuel cells good results was observed for cathode material of some perovskite.

Most common electrolyte are stabilized ZrO_2, Yttria stabilized-zirconia. It shows stability in both oxidizing and reducing atmospheres and also possesses good level of oxygen-ion conductivity at the operating temperature [43].

3.7 Catalysts

Catalyst changes the rate of a chemical reaction but recovered at the end of reaction. Positive catalysts increase the rate of reaction while inhibitors decrease the rate of reaction. Homogeneous catalysts are in the same phase with the reactants. Heterogeneous catalysts is solid and the reactants are gaseous or liquids.

Among several aspect of a green chemistry one is the use of solvent free reaction and use of heterogeneous catalysis is important. The development of efficient environmental benign process is one of difficult task for chemist in synthetic chemistry [44-45].

3.8Photocatalysis

A photocatalystabsorbs light to get excited to higher energy level and provides such energy to a reactant which to make a chemical reaction possible. Photocatalysts used for organic decomposition, for sterilization, water purification, air purification, and building exterior self-cleaning, particularly in areas where there is no electricity [46]. Photocatalytic organic degradation in water using ZnONPs has been recently reported [47]. Photocatalysts kill bacteria, viruses, fungi, cancer cells and also decompose the cells. Photocatalysts are typically made of metal oxides, oxysulfides, oxynitrides, metal sulfides, and their composites [48]. Metal oxides such as TiO_2 [49], doped metal oxides like Ni supported Ga_2O_3, Fe-doped TiO_2 [50], Mn doped ZnO, and composite metal oxide like Cu_2O/CeO_2 and mixed metal oxide such as $NiTiO_3$, $FeTiO_3$, and $CoTiO_3$ used as photocatalyst.

In the recent years, interaction between ultraviolet radiation and semiconductor catalyst is important method for mineralization of organic water pollutants [51]. Visible light-induced photocatalyst has more significance because main part of solar light is occupied by visible light. The photocatalyst involved itself in the chemical transformation and changes the rate of reaction. Photocatalyst is activated by appropriate energy photons whereas thermal catalyst is activated by heat.

4. Conclusion

There is need to develop efficient environmental benign methodologies for newer heterogeneous reusable catalyst without solvent. Heterogeneous catalysis and solvent free reaction instead of volatile organic solvents are highly important. Few perovskites behaves good cathode materials with high temperature solid oxide fuel cells still there is need to the reduce operating temperature of the SOFC. In such situation, we understood that, there is need to develop new heterogeneous catalyst that can be used to remove pollutants from aqueous medium by potocatalyst. The environmental and economic pressures have emphasized the need for efficient photocatalyst. These photocatalyst utilizes only the photon in wavelength less than 380 nm, that covers nearly 4 % of the solar spectrum, due to the large band gap. The areas that have received wide attention for innovative research are: (i) To enhance efficacy different metal oxide should be synthesized by innovative ecofriendly and economic method. (ii) Modification of metal oxide catalysts by doping with different metals iii) To develop combined degradation technique viz. biodegradation combined to photocatalysis, and iv) Study the catalytic effect on photocatalytic degradation, organic conversions such as oxidation, and cyclization at different reaction condition.

The brief review of earlier work shows that most of the photocatalyst of the type ZnO, PbO, TiO_2 etc. are checked for photocatalytic behavior and little attention was given on modified catalyst. The present work was undertaken to see the application of modified photocatalyst of the type ABO_3 like $AMnO_3$, $BSnO_3$, $CSiO_4$ and CAl_2O_5 where A, B, and C are different metals like Pb, Cu, and Mn for photodegradation of organic dyes. In the present study attempt is made to increase the efficiency of photodegradation as a function of concentration (dye), and amount of catalyst. Significance of photocatalytic treatments are that it does not show phase transfer but it give complete transformation of organic molecules.

References

[1] Catalyst, IUPAC Compendium of Chemical Terminology, (2009).
[2] Louise Lerner, 7 things you may not know about catalysis, Argonne National Laboratory, (2011).
[3] Laidler K. J. and Meiser, J. H. Physical Chemistry, (1982) 425.
[4] The 12 Principles of Green Chemistry, United States Environmental Protection Agency, (2012) 04-30.
[5] Tagusagawa C., Takagaki A., Iguchi A., Takanabe K., Kondo J. N., Ebitani, K., Highly active mesoporousNb-W oxide solid-acid catalyst. Angew. Chem. Int. Ed.49, (2010) 1128-1132.
[6] Kondo J. N., Yamashita T., Nakajima, K., Lu D., Hara M., Domen K., Preparation and crystallization characteristics of mesoporous TiO2 and mixed oxides. J. Mater. Chem.15, (2005), 2035-2040.
[7] Roggenbuck J., Schafer H., Tsoncheva T., Minchev C., Hanss J., Tiemann M., Mesoporous CeO2: synthesis by nano casting, characterization and catalytic properties. MicroporousMesoporous Mater.101, (2007), 335-341.
[8] Kuzushita K., Morimoto S., Charge disproportionation and magnetic properties in perovskite iron oxides, Phys. B Cond. Matter.329, (2003) 736-7.
[9] Misono M., A view on the future of mixed oxide catalysts: the case of heteropolyacids (polyoxometalates) and perovskites, Catal. Today, 100, (2005), 95-100.
[10] Snijkers F. M., Buekenhoudt. A., Luyten. J. J., Proton conductivity and phase composition in $BaZr_{0.9}Y_{0.1}O_{3-\partial}$, Scr. Mater.50, (2004), 655-9.
[11] Shin S., Yonemura M., Ikawa. H., Order-disorder transition of $Sr_2Fe_2O_5$ from brownmillerite to perovskite structure at an elevated temperature, Mater. Res Bull, 13, (1978), 1017-21.
[12] Tanasescu S., Totir N. D., Marchidan D. I., Thermodynamic properties of the $SrFeO_2$.5 and $SrMnO_2$.5brownmillerite like compounds by means of EMF-measurements, Solid State Ion, 134, (2000), 265-70.
[13] Zhang G. B., Smyth D. M., Defects and transport of the brownmillerite oxides with high oxygenion conductivity $Ba_2In_2O_5$, Solid State Ion., 82, (1995), 161-72.
[14] Libby W. F., Promising catalyst for auto exhaust, Science, 10, (1971).
[15] Powell A. V., Gore J. G. and Battle P. D., Journal of Alloys and Compounds, 201, (1993) 73-84.
[16] Chu M. S., Rae A. W., Manufacturing dielectric powders, Am. Ceramic. Soc. Bull., 74, (1995), 69-72.
[17] Hu Y. H., Harmer M. P., Smyth D. M., Solubility of BaO in BaTiO3, J. Am. Ceramic. Soc., 68, (1985), 372–6.
[18] Buscaglia M. T., Bassoli M., Buscaglia V., Alessio R, Solid-state synthesis of ultrafine Ba-TiO_3 powders from nanocrystalline $BaCO_3$ and TiO_2, J. Am. Ceramic. Soc., 88, (2005), 2374-9.
[19] D´Souza L., Richards R., Synthesis of Metal-Oxide Nanoparticles: Liquid-Solid Transformations in Synthesis, Properties and Applications of Oxide Nanoparticles (Rodríguez J. A., Fernández-García M., Eds.). Whiley N. J., Chpt.3, (2007).
[20] Suslick K. S., Choe S. B., Cichowlas A. A., Geenstaff M. W., Nature, 353, (1991), 414.
[21] Chen J. F., Wang Y. H., Gou, F., Wang X. M., Zheng C., Ind. Eng. Chem. Res.39, (2002), 948.
[22] Interrante L. V., Hampen-Smith, M. J., Chemistry of Advanced Materials: An Overview, While-VCH: New York, (1998).
[23] Uskokovick V., Drofenik M., Surf. Rev. Letter, 12, (2005), 239.
[24] Joo J., Park K. T., Kim B. H., Synthetic Met., 7, (2003), 135-136.
[25] Lee G. Y., Song R. H., etal, J. Electroceram., 17, (2006), 723.
[26] Song Y. L., Tsai S. C., Chen C. Y., Tseng T. K., Tsai C. S., Chen. J. W. and Yao Y. D., J. Am. Ceram. Soc., 87 (2004), 1864.
[27] Kang Y. C. and Park S. B., J. Mater. Sci., 31, (1996), 2409.
[28] Milosevic O. B., Mirkivic M. J., and Uskokovic D. P., J. Am. Ceram. Soc., 79, (1996), 1720.
[29] Katsuki A. H., Komarneni S., Microwave-hydrothermal synthesis of monodispersed nanophase α-Fe2O3, J. Am. Ceramic Soc., 84, (2001), 2313-7.
[30] Komarneni S., Li Q., Stefansson K. M., Roy R. Microwave-hydrothermal processing for synthesis of electroceramic powders. J. Mater. Res., 8, (1993), 3176-83.
[31] Komarneni S., Li Q. H., Roy R., Microwave-hydrothermal processing for synthesis of layered and network phosphates. J. Mater. Chem., 4, (1994), 1903-6.

[32] Komarneni S., Li Q. H., Roy R. Microwave-hydrothermal processing of layered anion exchangers. J. Mater. Res., 11, (1996), 1866-9.
[33] Microslaw M., Bucko J. O., J. Eur. Ceram. Soc., (2007), 27, 3625.
[34] Biasotto G., Simoes A. Z., Foschini C. R., Antonio S. G., and Varela J. A., Processing and Application of Ceramics, (2007), 5, 171.
[35] Elwin G., Parkin I. P., Bui Q. T., Baequin L. F., Pankhurst Q. A., Komarov A. V., and Morozov Y. G., J. Mater. Sci. Lett.16, (1997), 1237.
[36] Sathitwitayakula T., Kuznetsov M. V., Parkin I. P., Binionsc R., Mater. Lett.75, (2012), 36.
[37] IUPAC, Compendium of Chemical Terminology, 2nd ed. (the Gold Book) (1997).
[38] Goldstein, G. I., Newbury D. E., Echlin, P., Joy D. C., Fiori C., Lifshin E., Scanning electron microscopy and x-ray microanalysis. New York: Plenum Press, (1981).
[39] Coats A. W., Redfern J. P., Thermogravimetric Analysis: A Review, Analyst.88, (1963), 906-924.
[40] Liu X., Yu W., Evaluating the Thermal Stability of High Performance Fibers by TGA, Journal of Applied Polymer Science.99, (2006), 937-944.
[41] Jacob C. K., Gilbert, Slusarenko, Alan, Winyard, Paul G., Burkholz, Torsten (eds.), The Modern Art of Identification of Natural Substances in Whole Plants, Recent Advances in Redox Active Plant and Microbial Products, Springer Netherlands, (2014), 31-94.
[42] Dass, Chhabil, Hyphenated Separation Techniques, Fundamentals of Contemporary Mass Spectrometry, John Wiley & Sons, Inc., (2007), 151-194.
[43] Fu X. Z., Melnik J., Low Q. X., Luo J. L., Chaung K. T., Sangar A. R. and Yang Q. M., Int. J. Hydrogen energy., (2010), 11180.
[44] Yeong K. M., Tomoya K., Toshiyuki M., and Nobuhito I., Catalysts, 3, (2013), 646.
[45] Maurahashi S. I., Pure Appl. Chem., 64, (1992), 403.
[46] Ye J., Zou Z. and Matsushita A., Int. J. Hydrogen energy., 28, (2003), 651.
[47] Chakrabarti S, Dutta B. K. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. J Hazard Mater, 112, (2004), 269–78.
[48] Xu Y, Jia J, Zhong D, Wang Y. Degradation of dye wastewater in a thin-film photo-electrocatalytic (PEC) reactor with slant-placed TiO_2/Ti anode. J. Chem. Eng., 150, (2009) 302-7.
[49] Hung-Lung Chou, Bing-Joe Hwang, Chia-Liang Sun, New and Future Developments in Catalysis Batteries, Hydrogen Storage and Fuel Cells (2013), 217-270.
[50] Chen YS, Crittenden JC, Hackney S, Sutter L, Hand DW, "Preparation of a novel TiO_2-based p-n junction nanotubephotocatalyst" Environ SciTechnol, 39, (2005), 1201-8.
[51] Haque MM, Muneer M, Bahnemann DW. Semiconductor-mediated photocatalyzed degradation of a herbicide derivative, chlorotoluron, in aqueous suspensions. Environ SciTechnol, 40, (2006), 4765-70.