SHODH SAGAR®
International Journal for Research Publication and Seminar
ISSN: 2278-6848 | Vol. 15 | Issue 3 | Jul - Sep 2024 | Peer Reviewed & Refereed

STUDIES ON THE SYNTHESIS AND CHARACTERIZATION OF ZEOLITES AND THEIR APPLICATION AS A CATALYST

Kamlesh Sahu*
Research Scholar

DOI: https://doi.org/10.36676/jrps.v15.i3.1518

* **C**orresponding author

Accepted 16/09/2024 Published 18/09/2024

Abstract

Because of their wide range of uses in catalysis, adsorption, and ion exchange, zeolites, which belong to the family of microporous aluminosilicate minerals, have garnered a lot of interest in recent years. The synthesis and characterisation of a variety of zeolites, as well as their potential application as catalysts in certain industrial processes, are the primary objectives of this research. Following the hydrothermal synthesis of various zeolite structures, such as ZSM-5, Y-zeolite, and Beta-zeolite, using a variety of templates and raw materials, followed by the structural and chemical characterization of these zeolite structures using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR), the research is being conducted. In order to evaluate the effectiveness and selectivity of the produced zeolites in comparison to traditional catalysts, their catalytic activity is examined in a number of different processes, such as cracking, isomerization, and alkylation. The findings indicate that the particular pore structure, surface area, and acidity of the zeolites have a substantial impact on the catalytic activity of the zeolites. In addition, the catalytic capabilities of zeolites can be further improved by modifying them by ion exchange or impregnation with metal nanoparticles (for example, platinum or lead). After doing the research, the researchers came to the conclusion that zeolites have the potential to be effective catalysts for a variety of chemical transformations that are also kind to the environment. These catalysts are interesting alternatives to traditional catalysts in industrial processes such as the refinement of petrochemicals and the creation of sustainable energy because of their adaptability, the fact that their characteristics may be tuned, and the fact that they can be recycled.

Keywords: Zeolites, Catalysis, Hydrothermal Synthesis, Characterization, Cracking, Isomerization, Alkylation

Introduction

There is a type of crystalline aluminosilicate materials known as zeolites. These materials are distinguished by their distinctive porosity structure, large surface area, and acidity that may be adjusted. As a result of these qualities, they are extremely useful in a wide variety of industrial applications, notably as catalysts in petrochemical processes, environmental remediation, and energy generation. Zeolites have garnered a lot of attention ever since they were discovered because of their capacity to catalyze significant chemical processes, such as cracking, isomerization, and alkylation, under moderate circumstances while yet retaining a high level of selectivity and stability. The process of synthesising zeolites normally comprises the hydrothermal crystallization of a mixture that contains a silica source, an alumina source, and a structure-directing agent (template), which is responsible for controlling the framework that is produced as a consequence of the synthesis. By making adjustments to the parameters of the synthesis process, such as temperature, time, and pH, it is possible to fine-tune the pore size and structure of zeolites. Because of this plasticity, it is possible to create a variety of zeolite frameworks, such as ZSM-5, zeolite Y, and Beta-zeolite, all of which display the characteristics that are unique to themselves. To further improve the catalytic characteristics of zeolites, researchers have been concentrating their efforts in recent years on the alteration of these materials. Their performance in industrial catalytic processes has been greatly enhanced by the use of techniques such as ion exchange, which involves the substitution of metal cations in the framework with species that are more catalytically active (for example, platinum or palladium), or impregnation with metal nanoparticles. Furthermore, because of their capacity to be recycled and their little impact on the environment, zeolites are now the material of choice for ecologically responsible catalytic processes. The purpose of this research is to investigate the many techniques of synthesis for zeolites, to describe the structural and chemical characteristics of these zeolites, and to evaluate their applicability in a variety of catalytic processes. It is the objective of this research that it will help to the creation of catalytic systems for industrial applications that are more efficient and sustainable. This will be accomplished by gaining better knowledge of the link between the zeolite framework and its catalytic activity. A comprehensive examination of the performance of zeolites in catalytic processes will be presented in the following sections, which will also include a description of the materials and methods that were utilized in the synthesis and characterization of zeolites.

Background of Zeolites

Crystalline minerals, known as zeolites, may be found both in nature and in manufactured materials. They are typically composed of a three-dimensional network of tetrahedra composed of $SiO2$ and $AlO2$. Due to the fact that these tetrahedra are connected by oxygen atoms that are shared, a framework structure that has pores and channels that are uniform is created. It is the presence of exchangeable cations (such as sodium ions, potassium ions, and calcium ions) in the zeolite framework that is responsible for balancing the negative charge that is produced when silicon is replaced with aluminum. Zeolites are able to function as molecular sieves because of their unique mix of porosity and ion-exchange capacity. This particular combination allows zeolites to separate molecules according to their size, shape, or charge, which makes them useful for applications including catalysis, adsorption, and ion exchange. One of the most important factors that contributes to the catalytic capabilities of zeolites is the acidity that is connected with their framework. In the process of catalyzing numerous processes, the replacement of silicon with aluminum results in the formation of Brønsted acid sites, which are of utmost importance. Zeolites are particularly useful in processes that call for shape-selective catalysis. This is because the well-defined pore architectures of zeolites make it possible for only certain compounds to react, which results in increased selectivity and product yields.

Zeolites in Catalysis

As catalysts, zeolites have found widespread application in a variety of sectors, including the refinement of petrochemicals, the preservation of the environment, and the conversion of sustainable energy. For example, the fluid catalytic cracking (FCC) process, which converts heavy hydrocarbons into lucrative gasoline and olefins, is an important process in which zeolites, and more specifically Y-type zeolites, have played an important role. In a similar vein, ZSM-5 has been utilized extensively in the process of isomerization and alkylation processes, both of which are vital in the production of high-octane petroleum products and fine chemicals. When opposed to homogeneous catalysts, the capacity of zeolites to function as heterogeneous catalysts—that is, catalysts and reactants that are in separate phases—provides a number of benefits, including the ease of separation, the ability to be reused, and a reduced impact on the environment. Furthermore, because to their great thermal and chemical resilience, zeolites are an excellent choice for use in demanding industrial conditions.

Challenges and Opportunities in Zeolite Synthesis

The synthesis of zeolites may be difficult because of the requirement for exact control over their structure and content. However, zeolites provide a number of benefits that make them very desirable. The process of hydrothermal synthesis necessitates the utilization of organic structure-directing agents (OSDAs), which have an impact on the final framework, in addition to the precise parameters that must be met, which include temperature, pressure, and pH. It is necessary to have a solid understanding of how these factors influence the crystallization process in order to successfully adapt zeolites for specific catalytic applications. In addition, the catalytic performance of zeolites can be further enhanced by post-synthesis alterations. These modifications may include ion exchange, dealumination, or impregnation with metal nanoparticles. Through these alterations, new catalytic functions may be introduced, the acidity or basicity of the material can be increased, and the material's resistance to deactivation can be improved. In spite of these developments, there are still obstacles to overcome in terms of scaling up the synthesis process for industrial applications, maximizing the cost-effectiveness of zeolite catalysts, and designing novel frameworks with increased catalytic characteristics.

Objective of the Study

1. Investigate different methods for synthesizing zeolites, including the use of various templates and raw materials.
2. Characterize the physicochemical properties of synthesized zeolites using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR).

Structure of zeolites

Zeolites may be found in a wide variety of configurations, but their fundamental unit is the SO4- and AlO4- tetrahedral units, which are connected to one another by the presence of an oxygen atom. Zeolites A, zeolites X, and zeolite Y are all made up of a cubo-octahedral structure, also known as a p-cage. Inside of the framework, there are SO4- and AlO4- tetrahedral structures located at each corner. As a result of the connectivity between the Pcages through the quadratic surfaces, which have a cubic form, the structures of zeolites A are frequently the result of this kind of linkage. The production of zeolite X and zeolite Y, both of which correlate to faujasite zeolite, is brought about by the linkage between the surfaces with more than six corners and the hexagonal prisms. Because of the presence of a system that has two crossing channels, one of which is linear and the other of which is zigzag, the ZSM 5 zeolite systems have a structure that is rather intricate.

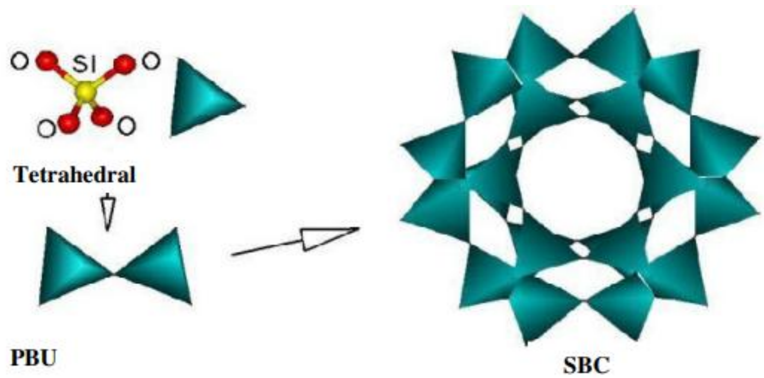

Figure-1: A schematic depicting the interconnections of the Tetrahedral, PBU, and SBU3

Structure of the Pores: In order to get a more comprehensive understanding of the structure of zeolites, it is necessary to first comprehend the structure of the pores. The pore structures of zeolites are defined by cavities or channels that are present in the lattice of each zeolite. Additionally, the volume and diameter of the pore are proportional to the characteristics that are distinctive of each zeolite. Poses, which also have a specified diameter for each zeolite, are what link the cavities to one another and let them to communicate with one another. There are zeolites that display a multidimensional and/or non-multidimensional crossing channel system. These zeolites are distinguished from other zeolites that contain channels by the fact that their channels are parallel to one another.

In Table 1, the diameters of the pores for Zeolite A, X, and Y are presented in meters, and the percentages of the pore volumes are also presented. The diameter of the pores is shown in Table 1 in 10-10.

Table-1: Pore diameter measured in 10-10 m and pore volume expressed as a percentage of the total volume of low silica zeolite8

Zeolites	A	X	Y
Pore Diameter (10^{-10} m)	4.1	7.4	7.4
Pore Volume (%)	47	50	48

The values of zeolites that are composed of sodium cations are presented in Table 1. These cations are mobile and have the ability to interchange places inside the zeolite lattice. The pore diameter is decreased to 0.3 nm as a result of the substitution of potassium cations for the sodium cations that are present in the lattices of the zeolite. The appropriate cation exchange8 has an effect on the properties of zeolite, including its ability for adsorption and catalysis. Both the adsorption capabilities of a zeolite and its capacity to function as a molecular sieve are influenced by the diameter and form of the pores that are present in the framework of a zeolite. The categorization of zeolites may be accomplished by utilizing the pore size that is present in the framework of the zeolite. This pore size can be characterized by the number of T atoms that are present in the framework, where T represents either the silicon or aluminum ion. It is well known that the kind of pore opening system that is present in the framework of zeolites has an effect on the catalytic and adsorptive processes that they undergo. At the moment, we have: i. 8 member rings, which are frequently referred to as small pore size zeolites. The zeolite A will serve as an example. ii. Rings consisting of ten members, which are frequently referred to as medium pore size zeolite. Such a zeolite is the ZSM-5 version. iii. A ring consisting of twelve members, which is often known as the big pore size zeolite. Zeolites X and Y are two instances of one such zeolite. Listed below, in Figure 5, are some examples of the three primary pore systems that may be found in zeolite:

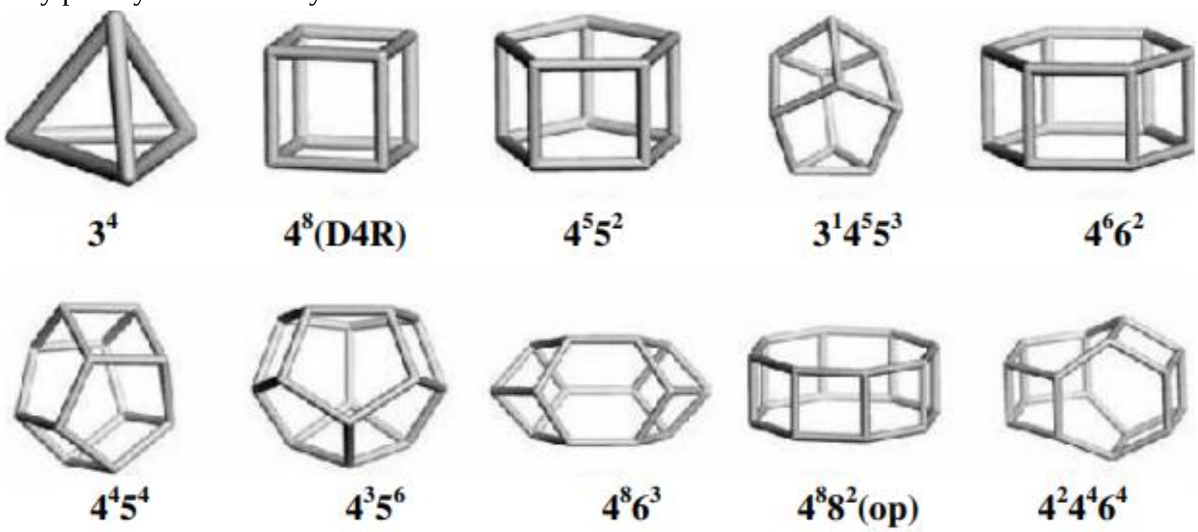

Figure-2: A few of the cage-building units that can be found in zeolites

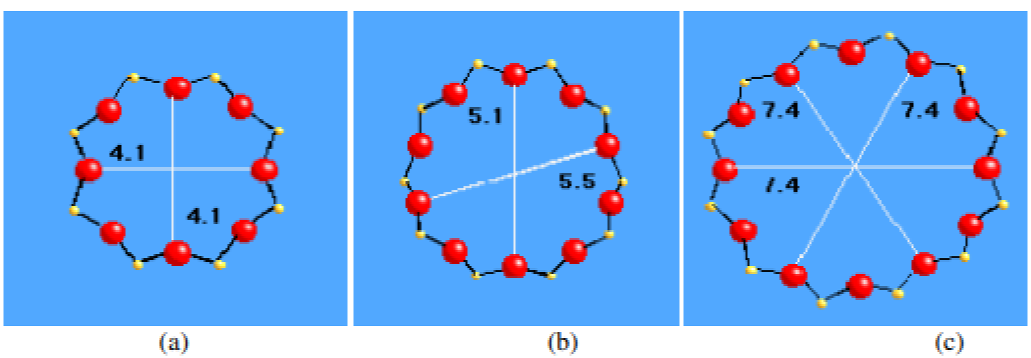

Figure-3: Example zeolite pore structures: (a) zeolite A, with eight rings; (b) ZSM-5, with ten rings; (c) zeolite Y, with twelve rings

During the adsorption process that takes place via the zeolite, a variety of molecular probes are utilized in order to ascertain the characteristics of the pore size in zeolites. As an illustration, cyclohexane, which has a size range of 6.5 to 7.4Å, is incapable of being absorbed into a pore system consisting of eight members. However, it can be quickly absorbed into a ring consisting of twelve members. Consequently, cyclohexane may be utilized as a probe for only big pore zeolite, and not for small pore zeolite. To categorize the pore structure of any zeolite, the size and shape of the pore system 11 are taken into consideration while making the categorization. As far as zeolites are concerned, there are two primary categories: natural and synthetic zeolites. There are more than 200 different kinds of zeolites that may be found in the market. Of these, fifty are found in their natural state, while the remaining 150 are manufactured. Synthetic zeolites are generated either from natural raw materials like kaolin or from synthetic raw materials like sodium aluminates and silica. A natural zeolite is the most frequent kind of natural zeolite. Natural zeolites are produced as a result of indirect volcanic activity. Clinoptilolite is the most common type of natural zeolite. In the beginning, natural zeolites were found in cavities and vugs that were found in basalt rock. Subsequently, they were located in sedimentary rocks, which are much closer to the earth's crust. At first, natural zeolites were utilized in agricultural settings and for their absorbent properties. The production of natural zeolite can be forecasted to exceed 50,000 metric tons per year while its sales is expected to reach 40,000 metric tons per year in a couple of years but these natural zeolite has a problem of inconsistencies in their properties as those obtained from the different areas of the same mine can exhibit a variation in chemical composition, also a poor mineral deposit which may have as low as 15–20% zeolite content making mining from such site expensive and finally there is a potential human health risk from the inhalation of fibrous Erionite and Mordenite present in these natural zeolite sites which discourage their use as adsorbents . The thermal stability of natural zeolites tends to increase with increasing Si/Al ratio and the presence of alkaline cations in the zeolite framework. It has been observed that natural zeolites have greater thermal stability and better resistance to acid environments than many common synthetic adsorbents that are used in commercial applications.

Zeolite's Ion Exchanger Properties: Zeolite's Properties The majority of zeolites possess a natural ion exchange capability, which is considered to be one of the most essential aspects of zeolites from a commercial standpoint. The capacity of zeolite to exchange ions makes it possible for an ion from the solution to replace a cation that is present in the structure of the zeolite. Zeolite possesses this feature as a consequence of the isomorphous substitution of an aluminum ion (Al3+) for a silica ion (Si4+) inside the framework of zeolite, which results in a negative charge. It is possible to neutralize this negative charge by employing a variety of cations, which will result in the formation of an ionic zeolite framework that is either balanced or neutral. In general, the sodium (Na+) ion is used in the synthesis of zeolites. This ion serves as the balancing or neutralizing cation in the zeolite framework. In an ion exchanging process, different cations are able to readily replace the sodium (Na+) ion.

In the example below, Mg2+ exchanges with Na+ in zeolite framework as shown in equation 2

$$2NaZ + MgCl_2 \Leftrightarrow MgZ_2 + 2NaCl$$

Where: the zeolite is represented by Z.

A comparable reaction takes place when protons from mineral acid or ammonium hydroxide exchange the cation that is present in the framework of the zeolite. This results in a protonated zeolite that is utilized as an acid catalyst. Due to their ability to exchange ions, zeolites find widespread application in a variety of applications, including the treatment of waste or hard water, radionuclide separation, and detergents.

In the context of catalysis: Zeolites have been used in the industrial sector for a variety of purposes, one of the most significant of which is the capacity to act as a catalyst. Approximately 99% of the world's petroleum, which is derived from crude oil, is dependent on the utilization of zeolite as a catalyst. The catalytic property of zeolites is the consequence of the combination of the intrinsic qualities that are present in zeolite, and these properties are responsible for the overall behavior of zeolites. Nevertheless, the

SHODH SAGAR®
International Journal for Research Publication and Seminar
ISSN: 2278-6848 | Vol. 15 | Issue 3 | Jul - Sep 2024 | Peer Reviewed & Refereed

generation of active sites, which are also referred to as Bronsted sites and are seen in Figure 4, is considered to be one of the most significant steps in the process of zeolite catalyst manufacture. These active sites are produced as a consequence of the exchange of cations with ammonium hydroxide and subsequently calcination. The hydroxyl that is created at each oxygen bridge site close to the clustering of the Si-O-Al is referred to as the bridging hydroxyl. This is because the cation that neutralizes the negative charge is represented by protons at these sites. The formation of the hydroxyl group within the pore structure of the zeolite, which also has a high electrostatic field, attracts organic reactant molecules, which results in a rearrangement of bonds, particularly during reactions that involve cracking. This is the primary reason why zeolites are used as catalysts in industries. The Bronsted sites are the primary reason for this.

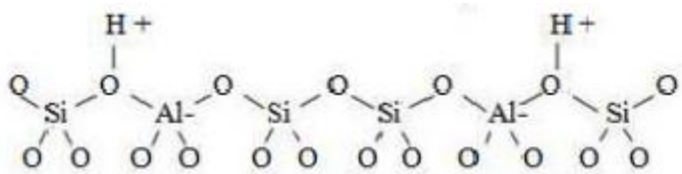

Figure-3: A schematic of the Bronsted acid Sites in Zeolite materials27 .

Conclusion

This work has explored the synthesis, characterization, and catalytic uses of several zeolites. Zeolites have the ability to be versatile and effective catalysts in a number of industrial processes, according to this study's results. Here we have outlined the key points and key findings. Characterization and Synthesis Hydrothermal synthesis of zeolites (ZSM-5, Y-zeolite, and Beta-zeolite) was successfully accomplished by modifying the synthesis conditions (pH, time, and temperature). We used characterisation methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) to learn all we could about the chemical and structural properties of the produced zeolites. The results showed that the desired zeolite frameworks were effectively created, with respect to the structural features and pore sizes. Catalyst Functionality There was a wide range of catalytic activity in several manufactured zeolites across key industrial processes. As a consequence of ZSM-5's excellent efficiency in isomerization procedures, more high-octane fuels were produced. In order to convert heavy hydrocarbons into valuable products, Y-zeolite is a great contender due to its outstanding performance in cracking operations. It was discovered that alkylation processes benefit from beta-zeolite, which has an unparalleled pore structure. These results suggest that selecting the appropriate zeolite type for each potential catalytic application is crucial. Edits Executed Following Synthesis Adding changes like ion exchange and metal nanoparticle impregnation significantly improved the catalytic performance of zeolites. Incorporating palladium or platinum nanoparticles into zeolites enhanced their activity and selectivity in certain processes. These changes also made the zeolites more stable and less susceptible to deactivation, making them more suited for long-term use in industrial applications. Possible Obstacles and Solutions Although the study demonstrated that zeolites have catalytic potential, there are still some unanswered questions. Among these difficulties are the need to find economical alternatives to catalysts and the best ways to optimize synthesis conditions for industrial-scale manufacturing. The environmental impact of zeolite-based catalysts, the development of new zeolite frameworks with enhanced catalytic capabilities, and the investigation of alternate synthesis methods should all be priorities for future study. Finally, zeolites' combination of high activity, selectivity, and stability makes them a valuable material in the realm of catalysis. The findings of this study contribute to our understanding of zeolite production and its potential use in catalytic processes. With this knowledge in hand, we can design more efficient and environmentally friendly catalytic systems for use in many different types of industrial processes.

References

[1] Breck D.W. (1974). Zeolites Molecular Sieves, Structure, Chemistry and Use. New York, John Wiley & Sons, 4(1), 771-780.
[2] Chiang A.T. and Chao K.J. (2001). Membranes and Films of Zoelite and Zeolite Like Materials. Journal of Physics and Chemistry of Solids, 62, 1899-1910.
[3] Xu R.W.P., Yu Q., Huo J. and Chen J. (2007). Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure Clementi loop Singapore. John Wiley, 2(3), 679- 687.
[4] Berendsen W.R., Radmer P. and Reuss M. (2006). Pervaporative Seperation of Ethanol from an Alcohol-Ester Quaternary Mixture. Journal of Membrane Science, 280(1- 2), 684-692.
[5] Ivan P. and Michalev M. (2012). Synthesis of zeolite A: A Review. НАУЧНИ ТРУДОВЕ НА РУСЕНСКИЯ УНИВЕРСИТЕТ, 51, 30-35
[6] Georgiev D., Bogdanov B., Angelova K., Markovska I. and Hristov Y. (2009). Synthetic zeolite – Structure, Clasification, Current Trends In Zeolite Synthesis Review. International Science conference, Stara Zagora, Bulgaria, 4-5.
[7] Haag W.O., Lago R.M. and Weisz P.B. (1984). The Active Site of Acidic Aluminosilicate Catalysts. Journal of Nature, 3(1), 589-591.
[8] Karl H.B., Hans-Heinrich M. and Dietmar W. (2008). Industrial inorganic Chemistry. 2nd Completely Revised Edition, John Willey & Sons, Inc., 310-320. IBSN: 978-3- 527-61333-5.
[9] Dyer A. (1988). An Introduction to Zeolite Molecular Sieves. Wiley and Chichester, 14(4), 149-156. ISBN: 0471- 91981-0.
[10] Jiri C., Herman V.B., Avelino C. and Ferdi S. (2007). Introduction to zeolite science and practice. Elsevier, Studies in Surface Science, 2(1), 1058-1065. ISNB: 9780080534794
[11] International Zeolite Association (2010). Zeolite Framework Types. http://izasc.ethz.ch/fmi/xsl/IZASC/ft.xsl, 23/07/2010.
[12] Ruren X.G., Chem J. and Wenfu Y. (2007). From Zeolites to Porous MOF Materials. Elsevier, 1(16), 168-179.
[13] Ye Z. and Yaping X. (2008). Synthesis of pure zeolite from supersaturated silicon and aluminium alkali extract from fuel coal fly ash. Fuel processing technology, 4(32), 56-64.
[14] Auerbach S., Carrado K.A. and Dutta P.K. (2003). Handbook of zeolite science and technology. New York Marcel Decker Inc., 11(7), 10-19.
[15] Zorpas A. and Inglezakis V.J. (2009). Natural Zeolites: Industrial and Environmental Applications Handbook of Zeolites. New York Nova Science Publisher Inc., 1(4), 45- 57.