PROBLEMS AND CHALLENGES OF SYNTHESIS OF ZEOLITE AND ZEOLITE-LIKE MICROPOROUS MATERIALS IN NIGERIA

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ABSTRACT

In the last few years considerable effort has been made targeted at the synthesis of zeolite and zeolite-like microporous materials with predetermined physicochemical and catalytic properties. However the position of Nigeria in this global feat cannot be easily defined hence the need for this paper. The problems of zeolite synthesis in Nigeria were highlighted. This is due basically to the non-availability of equipment to conduct detailed analysis of the raw materials and product as well as lack of technical know-how in the area of zeolite synthesis. Also the absence of common platform for zeolite scientists and technologist for cross fertilization of ideas is another set-back. In this paper, solution were also proffered which if well implemented will launch Nigeria into the amazing world of zeolite and its applications.

INTRODUCTION

It's an exciting and innovative time for all scientists and technologists working in the field of zeolite chemistry and applications. One of the positive repercussions of the recent rationalization within industry of their R & D effort in zeolite has been the creativity and generation of new ideas. For the last three decades the fortunes of zeolites and related materials has been very closely linked to their important bulk applications within the chemical process industry. Indeed without this support such a large and diverse academic community working in this field could not have been supported. However, zeolite and related porous materials form a unique class of well-ordered microporous solids with properties which inadvertently qualify zeolite to many other potential applications ranging from batteries to pharmaceutical products development. However zeolite research and development and hence its applications in Nigeria have being abysmally slow despite her natural endowment and potential to be a leader in the production of zeolite in Africa and perhaps with time in the whole world. Zeolite is very important material that makes any investment in its synthesis very justifiable. There are three basic properties of zeolite that makes its synthesis very paramount. These include its selectivity, adsorption and catalytic activity (Kovo, 2005).

Zeolite is widely used as catalyst especially in petroleum refining. They are also used as drying agent in separation process and as laundry detergent in wastewater treatment and nuclear effluent (Bekkum et al 1991). Other advanced application of zeolite is as components in membranes and sensor (Behrein, 1996). There is the need therefore for the local production of different types of zeolite because of the aforementioned uses and

applications, especially now that Nigeria spends a lot of her foreign exchange earning on the importation of zeolite to service her refinery (Kovo, 2005). The knowledge about the structure of these materials is essential for the understanding and prediction of their macroscopic physicochemical properties. Size and interconnectivity of the pores of zeolite and its cavities determine their molecular sieving capabilities (Natasa et al, 1999) and chemical composition and distribution of the framework which are important for catalytic, absorption and ion-exchange capacity. Determination of these important parameters or even distribution of metal atoms on the active site of the zeolite normally requires the application of newly developed instruments which presently are not available in Nigeria implying therefore that any meaningful research into the world of zeolite in Nigeria is in jeopardy.

Recent Global Development in Zeolite Synthesis

Hydrothermal synthesis of the majority of Zeolite-like material is based on the template molecules as structure directing agents (Davies et al , 1992).They incorporate in the structure pore openings during the synthesis and are subsequently removed by thermal treatment or soft chemical routes to obtain a microporous material. Recent advances in the hydrothermal synthesis of zeolite and zeolite-like material have been based on the new synthesis routes that have become better directed by the use of careful chosen template or structure - directing agents, sometime synthesized specifically so as to induce a particular pore geometry. Using a design strategy concerning template charge, shape and framework-template interaction, it has already been possible to synthesize a series of open-framework:
(1) Pure phase structure with
(2) Novel compositions and
(3) Controlled framework charges.

The first example of recently developed *de novo design* resulted in the development of a new microporous large pore magnesium aluminophosphate STA-1 with 12- member ring channels in one direction and low framework density. It was prepared hydrothermally using linear diquinuclidinium ions $[(C_7H_{13}N)\text{-}(CH_2)_n\text{-}(NC_7H_{13})]^{2+}$, n = 7,8,9, which possessed flexible, charged and bulky end to form structure with interconnected pore space.

There is currently a growing demand for Zeolite-like molecular sieves with larger pore size and retained shape selectivity (Davies, 1997). Quite a few extra-large pore size molecular sieves were successfully obtained in metallophosphate systems during the last ten years, such as $AlPO_4$-8 with 14-member ring channels etc, however most of them are thermally unstable and additionally all of the materials contain channels with the largest pore size in only one dimension. An approach to prepare materials for industrial application with multidimensional channel system and large cage like the most widely used catalysts zeolite X and Y (FAU) with multidimensional 12-ring channel system was reported recently (X.Bu et al,1997). Exploitation of novel or modified media for the crystal growth and preparation of large- pore microporous materials has been notably

progressing in the last few years. Addition of anions, particularly fluoride ions, into reaction mixture, assuming their directing and templating roles and beneficial effects on nucleation and crystal growth rate, has led to a new structure, such as the well known gallophosphate cloverite. Another interesting approach is the use of reverse micelles as nucleation sites in the synthesis of zincophophate with sodalite and faujasite topology (Castagnola, 1998). The urge for silica-based zeolite materials synthesis is based on the fact that they usually have much higher thermal stability as catalysts than phosphates. Until recently, the faujasite 12-ring channels were the largest among the silica-based materials.

The first silica based- material with 14-member ring channels were UTD-1, synthesized in 1996. The material which possesses one dimensional channel system is thermally stable up to 1000^0C. This led to the conclusion that the extra-large pore rings are not the major causes for the thermal instability of porous materials. CIT-5 of which 14-ring channel and SSZ-42 are some examples of the newly synthesized large-pore silica-based structures. Another new class of zeolite-like material are titanosilicate molecular sieves which is exceptionally good catalyst. These unique catalytic properties, high activity and catalyst stability have led to series of works on the use of titanium substituted silicate- and phosphate based materials.

There are also other fields of extensive zeolite-like materials research. One of them is the synthesis of chiral framework structure for potential applications involving enantioseletive separation and catalysis and a typical example is zeolite β.

Problems Associated with Zeolite Research in Nigeria

Information on the structure, chemical, pore opening, catalytic properties etc of zeolite is essential for proper appreciation of it potential application. In order to give a balanced description of frequently complex zeolite material places high experimental demand upon any serious researcher who seek to use or improve the microporous material for dedicated purpose. In general, the characterization of zeolite has to provide information about

(i) its structure and morphology,
(ii) its ability to sorb and retain molecules and
(iii) its ability to chemically convert these molecules.

These properties are usually performed using the state of the art equipment. Some of these equipment are listed below even though the list cannot be said to be exhaustive. These include:

1. Electron Microscopy (EM)
2. Thermogravimetry (TG), Differential Scanning Calorimetry (DSC)
3. Temperature Programmed Desorption (TPD)
4. Vibrational Spectroscopy (VS)
5. X-ray Diffractometry (XRD)
6. X-ray Fluorescence Spectroscopy (XRF)
7. X-ray Absorption Spectroscopy (XRA)

8. X-ray Photoelectron Spectroscopy (XRP)
9. Differential Thermal Analyses (DTA)
10. Nuclear Magnetic Resonance (NMR)
11. Infra-red Spectroscopy (IR)
12. Scanning Electronic Microscopy (SEM).

In Nigeria, most of t the equipment used in the characterization of zeolite and zeolite-material are not readily available, this hinders any meaningful research in the area of zeolite synthesis. These equipment are quite expensive that most universities and research institutes across the country cannot afford. However those institutions that have few of the listed equipment, the equipment are either obsolete or they are completely broken down Therefore to carried out any meaningful work on zeolite, one may need to send samples abroad, this will surely take a lot of time and resources before result will be achieved.

Looking into the Future of Zeolite Research in Nigeria.

The importance of zeolite to the industrial development of any nation cannot be overemphasized; therefore certain actions must be taken by all concerned to maximize the benefit of zeolite towards the economic development of Nigeria. All stakeholders including government, universities, research centre, corporate bodies such as Shell Petroleum, Petroleum Technology Development Fund must come to together to establish a standard laboratory each in the six geopolitical region of the country. Six universities can be selected from the regions to serve as a base for the proposed zeolite laboratory where researchers, scientists can easily asses these facilities in order to have their sample analyzed. There is an urgent need for researchers in the field of zeolite to form Nigeria equivalent of British Zeolite Association or International Zeolite Association. These will seriously stimulate interest in Zeolite research, its unfortunate that such an association is not in existence in Nigeria, the so-call giant of Africa even when South Africa Zeolite Association has hosted an international conference on Zeolite organized by international Zeolite Association. There is also the urgent need for the introduction of Science/Technology of Zeolite as electives for both chemical engineering and chemistry students so as to enhance better understanding of the subject are- zeolite, synthesis and characterization and certainly, these will spur great interest in the synthesis of zeolite and whence solve the problems.

CONCLUSION

The synthesis of zeolite and its application have been discussed and are deemed very important to emerging economy such as Nigeria. Nigeria spends a lot of her foreign earning on the importation of zeolite catalyst to service her refinery; however the sourcing of zeolite locally will go a long in conserving our foreign exchange, Hence there is the need for concerted effort into zeolite research and development in Nigeria. On this note, there is a need for all the parties concerned most especially the government need to provide the enabling environment so that research in zeolite and can flourish.