NANO POROUS ZEOLITE, A REMEDIATE TO AIR POLLUTION

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Abstract

Zeolites are crystalline allumino silicates with general formula $M_{2/n}O.Al_2O_3.ySiO_2.wH_2O$ where *y* is 2-200, *n* is the cation valence and *w* represents the water contained in the voids of the zeolite. These are structurally complex, crystalline inorganic polymers based on an infinitely extending three-dimensional, four connected framework of AlO_4 and SiO_4 linked to each other by the sharing of oxygen ions. In most of the zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedra are assembled into secondary building units which may be simple polyhedral like cubes, hexagonal prisms or cubo-octahedra. However the final framework structure consists of distinct arrangementthat exhibits pore sizes from 0.3 A^0 to 20 A^0 (1 angstrong unit = 0.1 nm). In the present study the zeolites are utilized as an adsorbent to capture the desired pollutant. Zeolites can separate varied gasses under certain conditions without forming a chemical bond. Different zeilites with their unique pore sizes are used to fix the Green House Gases (GHGs). Important zeolites useful for such applications are mordenite, chabazite, erionite and cliptilolite. These zeolites can be made into sheets and utilized in the form of road side advisement boards. They can be made into sheets by three methods 1) by hydrothermal reaction on a pore substrate from an aluminosilicate gel, 2) by seed-promoted hydrothermal crystallization of the zeolitic layer (A.S.T.Chiang et al, 2001) and 3) Microwave hydrothermal method (Guijun yang et al, 2019).

Key words: Zeolites, Framework structures, Molecular Sieve, Air pollution, Green House Gases, Adsorption.

Introduction

The earth's atmosphere contains Green House Gases (GHGs) that act as protective layers and temperature regulators to the living organisms. But, an increase in volume of any of these gases or all the GHGs increases, the global temperatures increases which may leads to the melting of ice and thus increasing the waters levels of oceans. According the 4th Assessment report 2007 of Intergovernmental Panel on the Climate Change (IPCC), global surface temperatures increased by 0.74 ± 0.18^0C (1.33 ± 0.32^0F) during the 20th Century. In this context the world is now looking towards the remedies to control the emissions of GHGs.

Zeolite minerals were known to occur typically as minor constituents in vugs or cavities in basaltic and volcanic rocks (Fig.1). The zeolite framework structures contain intra crystalline or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange (Edith M, et al.,2010). In addition zeolites are used for molecular sieving. There are several physical and structural features of zeolites that can be exploited for the mitigation of air pollution. The microporous structure of zeolites provides space for adsorption of molecules. The crystalline nature of zeolites allows strict size discrimination, hence they are referred as molecular sieves (Muralikrishnan,R., et al, 2014). Zeolites can be modified to incorporate properties as per the requirement by replacing the cations with the ions possessing the same sign of charge. The negative aluminosilicate framework of zeolites necessitates the presence of neutralizing ion-exchangeable cations within the framework. These cations can influence adsorption, diffusion and catalytic properties of zeolites (Ackley,M.W., et al, 2003). The Si/Al ratio of the framework controls the number of cations and the hydrophilic nature of the zeolites (YongongZheng et al., 2012). Zeolite open structure framework consists of many channels and/or interconnected voids (Fig.2) of discrete size in the range of 0.3-20A^0. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation. These cations are elements typically from the IA and IIA group of periodic table (DimitarGeorgiev et al., 2009). Some naturally occurring zeolites are Erionite, Mesolite, Mordenite, Natrolite, Paranatrolite, Tetranatrolite, Scolecite, Thomsonite. The zeolites can be made into membranes to be used conveniently for the mitigation of air pollution.

Fig. 1 Natrolite

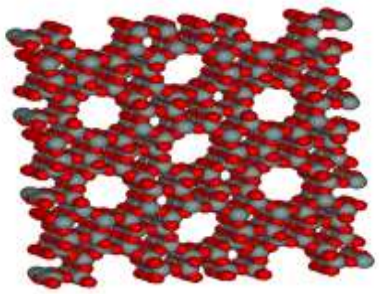


Fig.2 Microporous molecular structure of a zeolite

Methodology

The zeolite framework structures bear pore spaces in between, these can be changed by changing the ratio of AlO_4/SiOions (DimitarGeorgievet.al., 2009). Hence the zeolites can be used as molecular sieves for the removal of Green Houses Gases. The zeolites can be made into membranes with the same potential of molecular sieving action. The zeolite membranes can be prepared by three methods 1) by hydrothermal reaction on a pore substrate from an aluminosilicate gel, 2) by seed-promoted hydrothermal crystallization of the zeolitic layer (A.S.T.Chiang et al, 2001) and 3) Microwave hydrothermal method (Guijun yang et al, 2019). The zeolite sheets with specified pore sizes to capture a specific air pollutant with molecular diameter equal to the pore size fixed in zeolite (Fig.3 and 4) will kept at the road side. Later the captured air pollutant can be evacuated by the application of high pressure vacuum pump and can be collected in to a chamber and those gases can be utilized appropriately. Further the membranes can be reused in the same manner by erecting as road side sign boards.

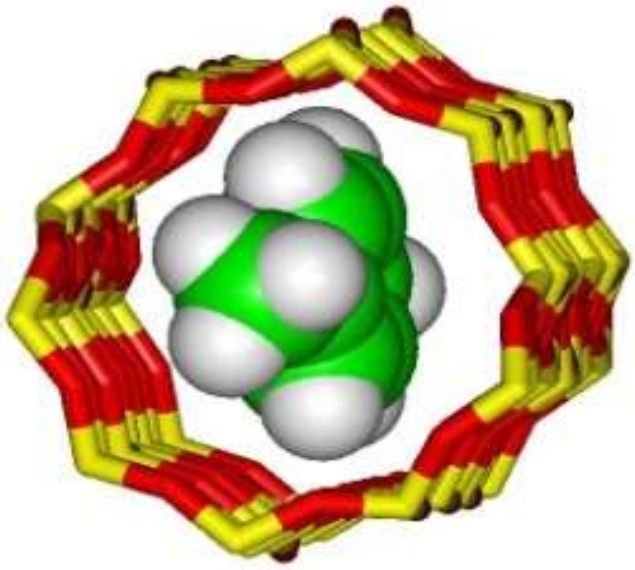


Fig.3 Zeolites capture (adsorb) gas molecules with weak forces

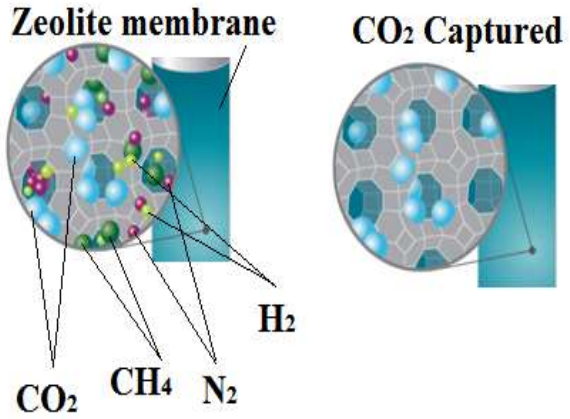


Fig.4 Zeolite membrane capture the desired pollutant

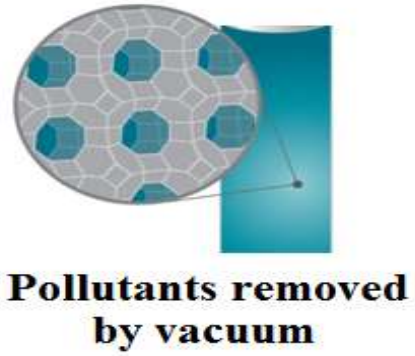


Fig.5 Pollutants remove by the application of pressure

Results and Discussion

Zeolites show an unique shape selective property which is the ability to adsorb preferentially certain molecules while excluding others. Zeolites can separate molecules based on differences of size, shape and polarity (Fig.3). Zeolites can be made into sheets by three processes.

Preparation of Zeolite Sheets

Hydrothermal reaction on a pore substrate from an aluminosilicate gel

In the Hydrothermal process initially a gel with the mixture of silicon, aluminum source in the presence sodium hydroxide mineralizing agent that helps to make a zeolite with desired structure. All these reactants dissolved in highly alkaline synthesis gel and heated in the autoclave from 90^0C to 200^0C, known as induction period. Later the nuclei start growing resulting a zeolite sheet (Reyes, M., 2014).

Seed-promoted hydrothermal crystallization of the zeolitic layer

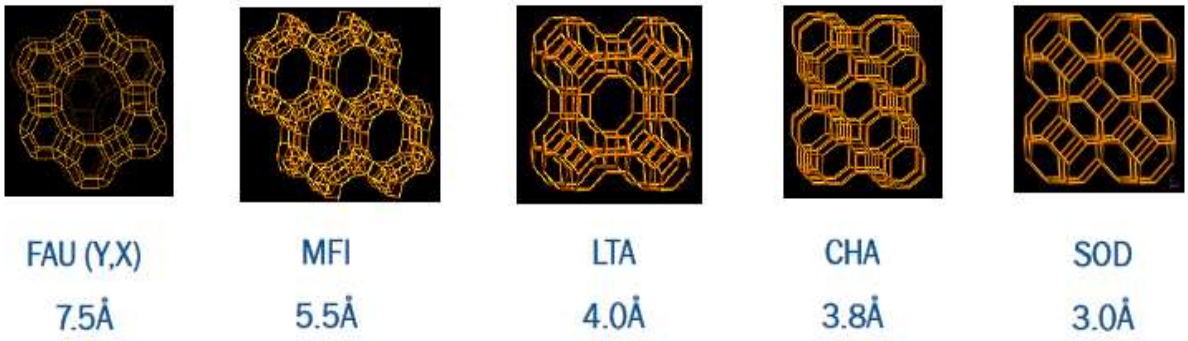
The process involves recrystallisation of substance under high temperature and high pressure. It follows five steps, initially the reactants silicon and aluminium source are dissolved in hydrothermal medium in the form of molecules, followed by the separation of these molecules due to the temperature difference between upper and lower portions of the container and the molecules are transported to low temperature region, where seed crystals start growing to form a supersaturated solution. Then the molecules are adsorbed, decomposed, desorbed. Later the material move to the margin point between high and low temperatures. At the end, the dissolved matter crystallizes (Guijun et al., 2019).

Microwave hydrothermal method

Microwaves when irradiated at a wavelength between 900 MHz and 2.45 GHz on the surface the reactant medium, it get penetrated into the medium and converted into heat energy. Due to this the molecular motion undergoes extreme changes resulting collision, friction and extrusion. The process generates zeolite crystals. When compared to the hydrothermal methods, the microwave assisted synthesis is faster, cleaner and more economical (Guijun et al., 2019).

The microporous structure of zeolites can be increased or decreased by replacing the cations with the ions possessing the same sign of charge. Thus the zeolites sheets can be prepared with desired molecular pore sizes. In this study it is proposed to utilize these zeolite sheets as flexi banners and sign boards along the road. For example CO_2 has a molecular diameter of 2.9 A^0which can be sequestered by the application of zeolite sheet of same pore size. Different air pollutants with varied pore sizes are given in Fig.6.

Fig. 6 Zeolites with their corresponding pore sizes



The air pollutants are of many types, each having different molecular diameter (Table–2).Hence Zeolite membranes of different pore size are used to remove different types pollutants. Zeolite membranes in the form of road side sign boards can be used in several stages, one membrane above the other. So that each membrane with unique pore size can absorb pollutants of corresponding molecular diameter.Molecules of some air pollutants are as follows.

Table – 2 Molecular diameters of some pollutants

Name of the Pollutant	Molecular Diameter A^0
Carbon dioxide	2.9
Carbon monoxide	2.8
Nitrogen	3.0
Hydrogen sulfide	3.6
Methane	4.0
Chloro di fluorimethane (Freon22)	5.3
Carbon tetrachloride	6.9

Conclusions

As per the IPCC report 2007 the increasing concentrations of GHGs is due to the fossil fuel burning and deforestation. The global warming effects include changes in the frequency and intensity of extreme weather events, species extinctions and changes in agricultural yields. In November 2009, 187 nations have signed and ratified the Kyoto protocol which is aimed at stabilizing the GHGs concentrations to prevent dangerous anthropogenic interference. Hence all the nations looking forward for a suitable remedy to sequester the GHGs. Global aforestation is one remedy to regulate further emission but for minimizing the existing excess GHGs, certain tool must be found. Application of nanoporous zeolites in the form of sheets and erection beside the roads in the form of advertisement boards is a good measure to capture the GHGs.

References

Ackley, M.W., Rege, S.U. and Saxena, H., (2003) Application of Natural Zeolites in the purification and separation of Gases, *Microporous and Mesoporous materials*, Vol.61, pp. 25-42.

Chiang, A.S.T., Keui-jung Chao (2001) Membranes nad films of Zeolite and Zeolite like materials, *Journal of Physics and Chemistry of solids* Vol. 62 pp. 1899-1910

DimitriosVogiatzis, NikolaosKantiranis, AnestisFilippidis, EvaggelosTzamos and Costas Sikalidis (2012) Hellenic Natural Zeolite as a Replacement of Sand in Mortar: Mineralogy Monitoring and Evaluation of its Influence on Mechanical Properties, *Journal of Geosciences* Vol. 2 pp. 298-307.

Edith, M. Flanigen, Robert W.Broach and Stephen T.Wilson (2010) Zeolites in industrial separations and catalysts, *Wiley. VCH Veriag GmbH &CoPublication.*

Guijun Yang and Soo-Jin Park (2019) Conventional and Microwave Hydrothermal sysnthesis and application of functional materials: A Review, Materials, Vol.12, pp. 1177.

Muralikrishnan, R., Swarnalakshmi, M. and Nakkeeran, E., (2014) Nanopartical-Membrane Filtration of Vehicular Exhaust to Reduce Air Pollution – A Review, *International Journal of Environment Sciences*, Vol. (4), pp.82-86.

Reyes Mallada (2014) Hydrothermal Synthesis of Zeolite, Srinter, DOI 10.1 007/978-3-642-40872-4_953-1.