Introduction

Generally, zeolite group are hydrated aluminum silicates and can be dehydrated and rehydrated without destroying their structure. If these minerals are surrounded by water, the sodium in them can be replaced by calcium or vice-versa. This could happen if calcium or sodium is present in sufficient concentration as in the water. This group of minerals has general formula (Na₂, K₂, Ca, Ba)(Al, Si)₃O₈n.xH₂O. Zeolite is a natural or synthetic hydrated aluminosilicate with an open three-dimensional crystal structure in which water molecules are held in cavities in the lattice. The water can be given off by heating and the zeolite can then absorb other molecules of suitable size (Burrows et al., 2013; Turkевич, 1967; Breck, 1974; Breck and Anderson, 1981; Barrer, 1978).

Zeolites have been used in chemical industries because of their unusual structures and properties, which are responsible for their use as catalysts, particularly in the petroleum industry (Breck and Anderson, 1981; Barrer, 1978; Barrer et al., 1959), as well as in conversion of simple organic molecules; as drying agents, and ion exchange. Zeolites are used for separating mixtures by selective absorption; for this reason they are often called molecular sieves. Zeolites are used as absorbents, as they absorb a wide range of molecules such as ammonia, and organic molecules as well as water. They are also used in sorption pumps for vacuum systems and contain types of processes, for example, in permutit, and ion-exchange like water-softening (Breck, 1974; Breck and Anderson, 1981; Barrer, 1978). The M⁺ ion, usually Na⁺, is the most common application of this ion exchange property in washing powders to allow the powder work well within hard water areas. When used as catalysts, the M⁺ is normally H⁺ and the zeolite acts as a strong acid. A similar ion-exchange process occurs when zeolite is used in the treatment of nuclear waste, where they remove radioactive, ⁹⁰Sr²⁺ ions (Burrows et al., 2013). They are also used in agriculture and at the nuclear energy industry. The cracking of crude oil and the conversion of alcohols to hydrocarbons are two examples of industrial processes that use zeolite as catalysts.

Zeolite catalysts are said to be ‘shape-selective’ as only molecules of specific sizes and shapes can fit into the cavities and react. Nevertheless, zeolites belong to the class of tectosilicates whose elementary structural units are tetrahedral, in which four oxygen ions are closely coordinated around the T-atoms, Fig. 1. As a general rule, the T-atoms are Si⁴⁺ and Al³⁺. However, the substitution of Si⁴⁺ by Ge⁴⁺ and of Al³⁺ by Ga³⁺ and B³⁺are common. The individual tetrahedra are always close to the regular geometry, but because the shared oxygen linkage can accommodate T–O–T angles from 130° to 180°, they can combine into a variety of framework structures. The primary building unit is the silica or alumina tetrahedron as shown in Fig. 1. These are linked by sharing of oxygen atoms. The geometric arrangement is such that Loewenstein rule is obeyed, which means that Al—O—Al bonds are
avoided (Barrer et al., 1959; Chu et al., 1985; Howden, 1985; Newsam, 1986; Meier, 1968). The replacement of tetravalent silicon ions at lattice positions with trivalent aluminium ions gives a net negative charge, balanced by compensating cations.

Fig. 1: Representation of SiO4 or AlO4 tetrahedron.

Meier, (1968) introduced the concept of secondary building units (SBU) which can be identified in zeolite structures. These units are the single–4–ring (S4R), the single–6–ring (S6R), single–8–ring (S8R), double–4–ring (D4R), double–6–ring (D6R), double–8–ring (D8R), 4–1 complex, 5–1 complex and 4–4–1 complex and are shown in Fig. 2 (Baerlocher et al., 2007).

Fig. 2: Secondary building units in zeolite framework

These units combine in different ways to give rings, the truncated octahedral and truncated cubic octahedral; these are the composites building units. For example, the truncated octahedron also known as the sodalite cage or β–cage contains 24 silicon (aluminium) tetrahedral and composed of six four–member rings and eight six–member rings (Fig. 3a, b, c). The free diameter of the cavity is 6.6Å. This framework type is found in sodalite. The original classification of zeolites based on these secondary building units, was able to define the seven groups and many more groups (Breck, 1974). Zeolite Y, for example is a Faujasite type zeolite and has a framework consisting of tetrahedral arrangement of sodalite units linked by hexagonal faces with six bridging oxygen ions resulting in spherical cavities or super cages. Each of these opens by common windows, distorted, 12–rings of 8.9Å diameter, into four identical cavities at the corners of a tetrahedron, Fig. 4(a) (Venuto and Landis, 1968; Jacobs, (1977).

Mordenite, (Ca, Na2, K2)Al2Si10O25.7H2O), Fig. 4b, has a two-dimensional, tubular pore system; the basic building consists of a ring of linked tetrahedra so that a system of large, elliptical, parallel channels, inter-connected by smaller cross channels is created (Spencer and Whittam, 1980; Meier and Meier, 1978; Kokotailo et al., 1978). A schematic representation of mordenite framework structure is given in Fig. 4(b). The ZSM-5 is a siliceous synthetic zeolite, used in the petroleum industry, has framework of 8–5–ring units that are linked together to form chains. The framework contains two intersecting channel systems; one sinusoidal tunnel system running along the b-axis and the other straight and running along the a-axis. Both channel systems have ten–membered ring elliptical openings about 5.5Å in diameter, Fig. 4(c).

Fig. 3: Structure of composite building units: (a) β–cage as in SOD (sodalite),(b) The 8–5 ring unit in MFI (ZSM–5) (c) MOR (mordenite) (Baerlocher et al., 2007).

Fig. 4: Schematic representation of (a) sodalite units in Y–zeolite, (b) mordenite framework structure (c) characteristic framework structure of ZSM–5 zeolite showing channel network (Baerlocher et al., 2007).
Zeolites Acidity and Activity

When zeolites are used as catalysts, the active sites involve separate phases such as metals oxides, occluded species and countervalent ions (Minachev and Isokov, 1976; Bravo et al., 1979; Rabo, 1976; Ben Tarrit and Che, 1980). Zeolite activity on the other hand is generally ascribed to both Brønsted and Lewis acid sites (Christner et al., 1968; Eberly, 1968). The Brønsted acid sites can be generated by several methods, such as direct exchange of the counter cation with protons from mineral acids. However this method has been shown to lead to surface dealumination, ammonium ion exchange, followed by thermal decomposition, to yield the hydrogen form hydrolytic processes, involving water coordinated to polyvalent cations (Dwyer et al., 1982; Rabo et al., 1961; Ward, 1968).

By reduction of appropriate counter ions, Lewis acid sites are thought of as Al–O species [AlO'] leached from the zeolite framework, because the Lewis sites are not stable at higher temperatures in the presence of water vapour (Kuhl, 1973; Jacobs and Beyer, 1979). The nature and strength of acid sites of zeolites have been investigated, these include base titration using Hammett indicators, temperature programmed desorption (TPD) of bases, N.M.R. and infrared spectroscopy (Ward, 1976; Mortier et al., 1984; Vedrine et al., 1979; Freude et al., 1974; Freude et al., 1977; Freude et al., 1982).

Shape Selectivity in Zeolites

For catalytic reactions within the active sites of zeolite crystals, the reactant must enter the pores of the zeolite and the products must diffuse out. The electronic field strength around the active site of a zeolite may play some steric requirements on reactant molecules, thereby affecting the electronic state of such reactant molecules. Shape selectivity can therefore be seen as molecular shape discriminating catalytic reactions. Three types of shape selectivity have been described and these are reactant selectivity, product selectivity and restricted transition state selectivity (Csicsery, 1976).

Reactant selectivity occurs when only a fraction of the reactant has access to the active sites because of molecular sieving effects, as demonstrated in dehydration of alcohols and hydrogenation of some alkenes (Weisz, 1980; Weisz and Friilette, 1960). Product selectivity occurs when only some product species with proper dimensions can diffuse out of the intracrystalline volume of the zeolite, due to differences in the diffusivities of product molecules, exemplified by the alkylation of methylbenzene over ZSM-5. Restricted transition state selectivity, occurs when certain reactions are prevented at the transition state or intermediate state leading to steric and space restrictions, for example in the disproportionation of o-xylene (Weisz, 1980; Derouane, 1980).

Zeolite synthesis

It must be pointed out at the onset that because of the variety of zeolite structures and synthesis methods, it will not be possible to provide in detail any particular method of zeolite synthesis procedure. These are however available (Robson, 2001; Georgiev et al., 2009). One of the many necessary requirements in zeolite synthesis is that the starting materials must all be pure chemicals otherwise impurities and contaminants will affect the crystallization process and cause nucleation of undesired species. The crystallization of the zeolitic material after preparation from solution generally follows a sequence of steps: nucleation of the phase, or phases, which is dictated by the composition of the solution and the growth of the nuclei to larger sizes by incorporation of material from the solution.

The general sequence of all zeolite synthesis experiments follows the pattern: Batch preparation; this is the actual quantities of materials plus the preparation steps used to prepare material for the crystallization step. Crystallization procedures; these are the experimental conditions and temperature profile which convert the finished batch to product slurry of zeolite crystals in a “mother liquor”. This is followed by product recovery, and characterization of product recovered.

The zeolite products, which are micron-sized crystals, are easily separated from the “mother liquor”, which is a solution containing excess alkali silicate, excess template, etc. by filtration or centrifugation. For reaction mixtures of low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, ratios, it is important to introduce anionic forms of aluminum such as sodium aluminate at the start of the reaction. Sodium aluminate is itself subject to formation of aluminum oxide hydrates when exposed to atmospheric carbon dioxide or during storage. It is therefore suggested that in order to prevent contamination, plastic containers such as polypropylene or Teflon should be used for the preparation of all solutions; for the reaction mixture, and for the crystallization, as the use of glass reaction vessels results in the leaching out of silica, alumina, and boron out of the glass and participating in the reaction.

Another important observation in zeolite synthesis involves the templating species. Alkali cations are most effective in templating low Si/Al zeolites from basic media. Quaternary ammonium cations are best at templating medium to high Si/Al zeolites and AlPO\textsubscript{4} based molecular sieves. Amines have been used to template AlPO\textsubscript{4}-based molecular sieves and high-Si zeolites. It is believed that the effective form of the amine is certainly the protonated form in AlPO\textsubscript{4}-based synthesis, and probably the protonated form even at the higher pH range typical of the high Si zeolites. Quaternary ammonium cations and amines have been very effective templates for phosphate-based structures, in general. The effectiveness, variety, availability, stability, and cost of the nitrogen-based cations as templates have not yet been rivaled (Robson, 2001).
**Aldol reaction**

Aldol is the name given to a class of reaction between an enol and enolates and carbonyl compounds. The base catalyst/hydroxide ion is regenerated in the last step; whereby, it is a catalyst. Aldol reaction is an important synthetic reaction because it leads to the formation of a carbon-carbon bond. It is a reaction that involves heating aldehyde or ketone under acid, or base-catalysis to form α,β-unsaturated ketone or aldehyde. This reaction involves a combination of nucleophilic addition and α-substitution steps. One partner, the nucleophilic donor is converted to its enolate ion, and it undergoes an α-substitution reaction when it adds as a nucleophile to the second partner, the electrophilic acceptor.

The product of aldol reaction contains a functional group capable of further transformation, thus providing access to a host of useful materials (McMurry, 2000; Loudon, 2002). For this reaction to occur, one of the starting aldehydes or ketones must have a α-hydrogen. The reaction is reversible, so to obtain good yields, the addition product must be removed from the reaction mixture as it is formed. In the base-catalysed aldol in reaction Scheme 1a, the base removes a proton from the α-carbon, forming an enolate ion. This enolate ion adds to the carbonyl carbon of a second molecule of the carbonyl compound and the negatively charged oxygen is protonated. The aldol addition is a nucleophilic addition reaction. The aldol addition products dehydrate to give unsaturated compounds. The double bond formed when the compound dehydrates is in conjugation with the carbonyl group. The conjugation increases the stability of the product making it easier to form.

The kinetics of this reaction is interesting in that at very low hydroxide ion concentration, the equation 1, which is the proton transfer step, is the slow step and thus rate-determining equation. This is so because the proton is being removed from a carbon atom. In the base-catalysed aldol reaction Scheme 1a, the base removes a proton from the α-carbon, forming an enolate ion. This enolate ion adds to the carbonyl carbon of a second molecule of the carbonyl compound and the negatively charged oxygen is protonated (Clayden et al, 2001; Carey and Sundberg, 2007; Casale et al., 2007; Anderson and Peters, 1960). These rate equations can be written as:

\[ \text{rate} = k_1[\text{CH}_3\text{CHO}][\text{OH}^-] \]  
Equation 1

\[ \text{rate} = k_2[\text{CH}_3\text{CHO}][\text{enolate ion}] \]  
Equation 2

\[ \text{rate} = k_3[\text{CH}_3\text{CHO}]^2[\text{OH}^-], \text{ where } k_3 = k_1 \times k_2 \]  
Equation 3

The aldol equilibrium generally favors condensation product in the case of aldehydes with no α-substituent (RCH\(_2\)CHO), but favors starting material for more highly substituted aldehydes and for most ketones. Steric factors are responsible for these trends, since increased substitution near the reaction site increases congestion in the aldol product. At higher hydroxide ion concentration, equation 2, which involves the enolate ion, becomes rate-determining equation. The overall rate equation can therefore be written as equation 3.

Generally, in synthesis low concentration of base is employed so that the aldol product is isolated, further reaction occurs by dehydration, to give stable conjugated unsaturated compounds. For example, the aldol product from acetaldehyde, 3-hydroxybutanal, gives but-2-enal, crotonaldehyde. The dehydration happens in basic environment as a second enolisation. Base-catalyzed aldol reactions sometimes give aldol elimination product as in equation 4. The reason for this, is based on the choice of conditions, the more vigorous conditions (stronger base, higher temperatures, longer reaction time) tend to give elimination product, also on the structure of the reagents. In acid-catalysed aldol reactions, the unsaturated product forms instead of the aldol products as elimination is easier as shown in scheme 1b and scheme 2.

**Discussion**

**Aldol Reactions in Zeolites**

From observation of scheme 3, zeolite catalysts provide alternative to conventional catalyst such as NaOH and H\(_2\)SO\(_4\) used in aldol reactions. This is because they possess both Brønsted and Lewis acid sites contained within their pores and channels. Their removal from the reaction mixture can be easy, and very small amounts are required for their catalytic action. In the process, aldol condensation as practiced over zeolite catalysts has been demonstrated by passing ethanal in the gas phase over ZSM-5, with a silica-alumina ratio of 26000 within the temperature range of 170 to 247°C. In this reaction, ethanal conversion to 2-butenal (crotonaldehyde) was 20%. Similarly passing acetone over ZSM-5 zeolite showed a 10% conversion in the temperature range 280 to 370°C to 4-methyl-3-penten-2-one (mesityl oxide). In addition to this, a product of further condensation to 2,6-dimethyl-2,5-heptadien-4-one (phorone) was observed (Dessau, 1991).

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Scheme 1: (a) Based-catalyzed, (b) acid-catalyzed aldol condensation reactions.

Scheme 2: Dehydration product obtained from acid-catalyzed aldol condensation reaction.
It is interesting to note that when acetone was passed over zeolite at temperatures below 200°C, no condensation product was observed. These reactions are illustrated in scheme 3. Other examples of aldol condensation reactions over zeolite catalysts and internal condensation reactions are shown in scheme 4 (Dessau, 1991; Shen et al. 2011; Dumitriu et al., 2001). In these mixed reactions, for example scheme 4 reaction (c), it was observed that the exiting gas from the reactor contained only 3.3% of p-methyl cinnamaldehyde, the mixed condensation product, 13.6% crotonaldehyde, and the condensation product of ethanol. In scheme 4 reaction (a), aldol reaction of ethanal and methanal over silicalite, ZSM-5 and Al, and Fe modified ZSM-5 zeolites; the conversion was found to be poor over silicalite-1, between 6 and 15%.

However, the mixed condensation product was found to be favored at temperature above 300°C and the self-condensation of ethanal to crotonaldehyde was favored at temperatures below 300°C (Dumitriu et al., 2001). It was noted that selectivity to acrolein increased with increase in temperature. An internal aldol condensation reaction was achieved by passing acetonylectone over ZSM-5 zeolite, silica-alumina ratio of 26000 at 350°C with the formation of 3-methyl-2-cyclopenten-1-one with 93% yield. When acetonylectone was passed through a ZSM-5 zeolite with a silica-alumina ratio of 600 at 350°C; a reduction in yield of 3-methyl-2-cyclopenten-1-one was obtained (89.1%). In a similar experiment at 350°C over a different zeolite, ZSM-11, with a silica-alumina ratio of 4600, the conversion to 3-methyl-2-cyclopenten-1-one was 90.6% in reaction over modified ZSM-5 zeolites. All these reactions considered the use of zeolites as acid catalysts in aldol reactions.

When different set of reactions zeolites were considered as base catalysts for aldol reactions and experimental results were compared with metal catalysed reaction (Shen et al., 2011). In these experiments, results obtained from zeolite NaY and Ni-NaY catalysed reactions were compared with results obtained from MgO-ZrO₂. The results discussed in terms of base-catalysis scheme 4 reaction (b) showed that the conversion to aldol products were very high but were significantly higher than values obtained in earlier considered reactions. The conversion over MgO-ZrO₂ material was very much higher than over the Y-zeolite catalysts.

Modification of the Y-zeolite with nitrogen showed increased conversion and it was suggested that replacement of the oxygen bridges by the less electronegative nitrogen increased the base strength of the zeolite framework. Change in the catalytic activity and product distribution in these reactions improved the conversion to aldol products, and selectivity to ‘monomer’. This report is in contrast to previous reports where water is regarded as a poison in aldol reactions (Dumitriu et al., 2001; Panov and Fripiat, 1999).

In all these reactions whether the zeolite is considered as acid or base catalyst, there was improvement in the conversion of reactants to aldol products over the modified zeolite. These improvements have been attributed to the nature and modification of the active site. For example going from silicalite-1 to ZSM-5 material with higher aluminum content, demonstrated this improved conversion, equation 5 (Dessau, 1991; Dumitriu et al., 2001). Silicalite-1 is known for its low acidity and weak acid sites. This is due to the small amount of Brønsted acid sites. When aluminum is incorporated into the framework the number of acid sites increases also the number of active sites increases, thus accelerating the condensation reaction.

![Scheme 3: Examples of aldol reactions carried out in ZSM-5 zeolite catalyst.](http://nepjol.info/index.php/IJASBT)
Scheme 4: Zeolite catalyzed mixed and internal aldol condensation reactions of aldehyde and ketone reaction (a), reaction (b), reaction (c).

Conclusion
It has been revealed that zeolites can function as catalysts in aldol type condensation reactions. It has also been concluded that weak acid sites as well as a small number of active sites favor the aldol condensation reaction of carbonyl compounds. It was suggested that both Brønsted and Lewis acids are involved in aldol reactions with Lewis acid sites the most probable catalytic sites. In this regard, it might be that we have to manipulate the acidity and acid sites in these zeolite materials to achieve these. Therefore, from this review, plans are on the way to exploits available zeolites and synthesize new zeolite type materials.

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