PRODUCTION OF HIGH GRADE SODIUM SILICATE AND SILICA SOL FROM KANKARA KAOLIN FOR ZSM-5 SYNTHESIS

BY

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DEPARTMENT OF CHEMICAL ENGINEERING
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DECLARATION

I declare that the work in this thesis entitled "Production of High Grade Sodium Silicate and Silica Sol from Kankara Kaolin for ZSM-5 Synthesis" has been performed by me in the Department of Chemical Engineering, Ahmadu Bello University, Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

Mustapha Yusuf	_____	_____
Name of Student	Signature	Date

CERTIFICATION

This thesis entitled "PRODUCTION OF HIGH GRADE SODIUM SILICATE AND SILICA SOL FROM KANKARA KAOLIN FOR ZSM-5 SYNTHESIS" by MUSTAPHA YUSUF meets the regulations governing the award of the degree of Master of Science (M.Sc) in Chemical Engineering of the Ahmadu Bello University, and is approved for its' contribution to knowledge and literary presentation.

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DEDICATION

To my LATE parents Alhaji Shitu Sani and Hajiya Rakiya Sani. May their gentle souls rest in perfect peace, ameen.

ACKNOWLEDGEMENT

I thank ALLAH ALMIGHTY Who, in His infinite mercy, favored me in life, among which is seeing me through this noble course and making my dream a reality.

I find it difficult to estimate the magnitude of my thanks to my LATE parents, for, whatever I achieve in life is the progeny of that you planted in me. I will live with happy memories of your support and always be grateful for your role in my life. May Allah reward you with Paradise.
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ABSTRACT

This research work utilized the silica obtained from locally sourced kaolin (from Kankara in Katsina State) to produce zeolite grade sodium silicate as a raw material for the preparation ofsilica sol for ZSM-5 synthesis. The work also involved development of sodium silicate pilot plant. Of the various dealumination routes considered, double dealumination, specifically 2.5/2.5 fold was regarded the best for its economic advantage and capability to completely remove alumina (Al_2O_3) alongside with the major trace contaminants like CaO and Fe_2O_3 associated with silica from kaolin. When the resulting silica was employed for sodium silicate preparation, 6.0M concentration of sodium hydroxide solution gave the highest dissolution (95%). However, it was not suitable for the preparation of the targeted silica sol due to its high silica content, hence 2.5 and 3.0M concentration of sodium hydroxide solution both with lower percentage dissolutions (77 and 78) were selected as the two that yielded the desired results for the silica sol preparation.

Kinetics of silica dissolution in sodium hydroxide were studied and it was found that it followed first order reaction law with specific rate constant of 1.7798min^{-1}. Although, three types of silica sols were prepared via peptization and ultra-sonication methods, basic sol produced by ultra-sonication method was the best for its superior qualities (stability and suitability for ZSM-5 preparation). Despite the fact that commercial zeolite grade silica sol was more concentrated, the prepared Kankara kaolin based silica sol was purer and the X-ray diffraction patterns of all the zeolites synthesized from these sols were purely crystalline and conformed well with both the standard and the commercial XRD patterns of Na-ZSM-5. The X-ray fluorescence of the powder products further classified the materials as high silica zeolites (silica to alumina ratio equal to 10 to several thousands). Though, Na-ZSM-5 from commercial silica sol has higher silica to alumina ratio theNa-ZSM-5 produced from Kankara kaolin showed fewer impurities. Based on

the information from the kinetics study at 90^{o}C, a sodium silicate pilot plant of approximately 10 liters capacity for a single batch in 3hrs was developed with a batch requirement of 5kg silica sand which gave a percentage yield of 88.4%.

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Abbreviations, Definitions and Symbols

A.B.U.: Ahmadu Bello University

Aggregation: A massing together or clustering of independent but similar units, such as particles, parts, or bodies.

Anisotropic: Unequal physical properties along different axes

ANSI 304 SS: Stainless steel 304

C_A: Concentration in mol per dm^3 at any time t

C_{A0} : Concentration in mol per dm^3 at time is equal to zero

Colloidal silica: More highly polymerized species or particles larger than about 50 Å, although sometimes down to 10-20 Å.

DD: Double dealumination

Dealumination: Leaching of alumina from meta-kaolin by the use of acid

Hydrogel: Dispersion of molecules of a liquid within a solid in which the solid is the continuous phase and the liquid is the discontinuous phase

Isotropic: Having physical properties that do not vary with direction

MG-Silicon: Metallurgical grade silicon

Orthosilicic acid: A soluble form of silica containing only one silicon atom and generally formulated as $Si(OH)_4$ also known as monosilicic acid.

Petization: A process responsible for the formation of stable dispersion of colloidal particles in dispersion medium (for example, water)

Polymerization: A process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks.

Polysilicic acid: Polymers with molecular weights (as SiO_2) up to about 100,000, whether consisting of highly hydrated "active" silica or dense spherical particles less than about 50 Å in diameter.

PTDF: Petroleum Technology Development Fund

SD: Single dealumination

Silica sol: May refer broadly either to polysilicic acid or colloidal silica

Silicic acid: A compound of silicon, oxygen, and hydrogen, regarded as the parent substance from which is derived a large family (the silicates) of minerals, salts, and esters.

Teflon: Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer that has numerous applications due to its non-reactive nature.

TEM: Transmission electron microscopy

TEOS: Tetraethyl orthosilicate $Si(OC_2H_5)_4$.

Ultrasonicator: A device use to disintegrate most cells, bacteria, spores or tissue. It can also disperse solids in liquids and degas liquids.

X: Percentage conversion

XRD: X-ray diffraction

XRF: X-ray fluorescent

Zeta potential: A scientific term for electro-kinetic potential in colloidal dispersions

ZSM-5: Zeolite Socony Mobil–5

θ: Theta

∞: Infinity

ζ : Zeta potential

CHAPTER ONE

1.0 INTRODUCTION

Silica is by far the most predominant component of the earth's crust, yet much remains to be learned of its chemistry and, in particular, its solubility behavior in water. The manner of its deposition to form such curiosities as quartz crystals containing mineral oil, mercury, or liquid carbon dioxide remains a mystery. Flint, which the remote ancestors recognized as the strongest and toughest stone available, was apparently formed in some instances from the siliceous skeletons of ancient sponges by a mysterious process of solution transport. Within some plants and marine organisms, soluble silica is transported and deposited in characteristic intricate patterns. Only recently has it been recognized that soluble silica, even in trace amounts, plays a role in the development of mammals, Iler (1979).

Colloidal silica is a stable dispersion of solid silica particles. It has found various applications such as casting, semiconductor wafer polishing, coating, and textiles, and it has also been used as an inorganic binder, a nano-sized filler, and as a catalyst precursor, Hyung et al (2010). For more than one century, colloidal silica has been applied in many industries, e.g. as binder for inorganic paint, stiffener for hard coating reagent and especially as abrasive particles. It is also been used in production of paper. Nearly, all of the processes which have been proposed and employed for producing colloidal silica use the low cost sodium silicate solutions as main raw material. These methods include dialysis, electro-dialysis, acid neutralization, peptization and ion exchange. Since the ion exchange method is the most easily controllable of the four methods, it is the most popular method for industrial production of colloidal silica nowadays. The homogenous nucleation and the surface growth play important roles in the mechanism of particle formation via ion exchange method, Karami et al (2008). This research work focuses on the preparation of

silica sol from Kankara kaolin for ZSM-5 synthesis and the development of sodium silicate pilot plant. The methods employed for the preparation of the silica sol were peptization and ultra-sonication methods due to their economic and technological advantages and the low temperature/pressure requirements.

1.1 Research Problem

High purity silica sol needed for the synthesis of ZSM-5 is normally produced from high technology processes; this limits its production to the technologically advanced countries.

Sodium silicate often used to prepare silica sol is produced from crystalline silica in a high environmental/conditions which is expensive. Thus, the need to devise a more cost-effective method.

1.2 Research Aim and Objectives

1.2.1 Aim

To produce high grade sodium silicate and silica sol from Kankara kaolin for ZSM-5synthesis.

1.2.2 Objectives

I. To establish the optimum de-alumination process parameters (specifically the amount of acid used and number of de-alumination) for meta-kaolin to obtain high purity silica.
II. To prepare sodium silicate from de-aluminated Kankara kaolin.
III. To develop a pilot plant for the production of sodium silicate.
IV. To study the process conditions for preparing silica sol from sodium silicate.
V. To determine the suitability of the silica sol obtained for the preparation of ZSM-5.

1.3 Scope of Work

I. Preparation of colloidal silica from sodium silicate obtained from Kankara kaolin
II. Development of a pilot plant for the production of sodium silicate from Kankara kaolin

III. Preparation of ZSM-5 using the colloidal silica

1.4 Justification

Presently, high quality ZSM-5 and the raw materials for its synthesis (especially silica) are always imported; this is the major factor behind the handful number of research going on in this area. Therefore, the outcome of this work, apart from encouraging more research in the area, will help toward complete indigenization of the zeolite production technology where by the raw material (kaolin) which is available in the country will be process and the zeolite prepared locally, hence this will create more job opportunities in the country and add value to the local raw material (Kankara kaolin). By extension, foreign exchange earnings would be saves.

CHAPTER TWO

2.0 LITERATURE SURVEY

2.1 Colloidal Silica

Despite the fact that colloidal silica has the same chemical formula as quartz sand, SiO_2, the two materials could hardly be more different in their effect on paper machine operations. The key difference is size. The sub-units of colloidal silica particles are typically in the range of 1 to 5nm. Whether or not these sub units are joined together depends on the condition of polymerization. Initial acidification of water-glass solution yields $Si(OH)_4$. If the pH is reduced below 7 or if salt is added then the units tend to fused together in chains. These products are often called "Silica gels" If the pH is kept slightly on the alkaline side of neutral, then the sub-units stay separated, and they gradually grow, these products are called silica sols, Iler (1979).

2.2 Silica-Water System

As water is a unique liquid, so also is amorphous silica a unique solid. They are much alike, both consisting mainly of oxygen atoms with the smaller hydrogen or silicon atoms in the interstices. As pointed out by Weyl et al (1964) "Some properties of water and silica are so similar that the transition between hydrated silicic acids and the aqueous matrix is a gradual one. It was concluded that water molecules are arranged in a rather open structure like quartz, and undercooled water has a still more open structure, like tridymite, Iler (1979). Another model has been proposed by Weres et al (1985). These ideas lead to the suggestion that there is some relationship between the density of water and the solubility of the various forms of silica, since both are related to the close packing of oxygen atoms. Both silica and water consist, from the standpoint of volume, largely of oxygen atoms, which are packed together with a characteristic packing density, the small hydrogen and silicon atoms tit between the oxygen atoms,

contributing little to the volume. In pure orthosilicic acid, $Si(OH)_4$ (if it could be prepared), the small silicon and hydrogen atoms, lying in the interstices between the large oxygen atoms, would be more or less evenly distributed throughout the mass. Polymerization of silicic acid to form solid silica and water amounts to separation into two phases: in silica, the silicon atoms surround themselves with oxygen atoms in a region of closer packing, and in water hydrogen atoms surround themselves with oxygen in a region of more open packing. In amorphous SiO_2, there are 1.17 grams of oxygen per cubic centimeter; in water of density 1.0, there is 0.89 gram of oxygen per cubic centimeter. There is no evidence that silica is "soluble" to any appreciable degree in any liquid other than water. However, that statement may depend on the definition of "soluble." The dissolution of silica involves a chemical reaction or hydrolysis in an excess of water:

$$SiO_2 + 2\,H_2O \rightleftharpoons H_4SiO_4 \quad \text{.....(2.1)}$$

Thus it is not a simple solution such as that of sugar in water, where the sugar molecule exists intact in solution as in the crystalline state. Instead, it is analogous to a hypothetical equilibrium of silica and ether in an excess of ether:

$$SiO_2 + 2\,(CH_3)_2O \rightleftharpoons Si(OCH_3)_2 \quad \text{..... (2.2)}$$

Since low condensation polymers such as $[(HO)_2SiO]_4$ appear to be clear water-miscible fluids resembling a polyhydroxy organic compound like glycerol, the monomer, "soluble silica" or $Si(OH)_4$, would probably be a clear liquid if it could be isolated in anhydrous condition. Ina pure state it might even crystallize. The unusual nature of the silica-water system has been noted by Kitchener et al (1955) who pointed out that the endless confusion in the literature concerning the silica-water interface has arisen because the hydration and solubility characteristics have not

been understood. For example, there is the question as to why silica sols are extraordinarily stable at pH 2 where the zeta potential ζ (the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle, a key indicator of the stability of colloidal dispersions) is zero and become increasingly sensitive to electrolytes at higher pH, where the potential is highest-in contradiction to the generally accepted electrical double layer theory. Another mystery is that crystalline quartz becomes coated with a film of amorphous silica even though the solution is undersaturated with soluble silica with respect to a surface of amorphous silica. The dissolution and deposition of silica in water involves hydration and dehydration reactions catalyzed by OH^- ions:

$$(SiO_2)\boldsymbol{x} + 2\,H_2O \underset{\text{dehydration}}{\overset{\text{hydration}}{\rightleftharpoons}} (SiO_2)_{x-1} + Si(OH)_4 \quad \text{.....(2.3)}$$

For massive amorphous silica, the equilibrium concentration of $Si(OH)_4$ at 25^oCcorresponds to 70ppm as SO_2. This is the "solubility" of anhydrous nonporous amorphous SiO_2. However, except for fused SiO_2 glass, the common forms of amorphous silica consist of extremely small particles of amorphous silica, or porous aggregates, the surface of which is hydrated as SiOH groups. These exhibit a somewhat higher solubility so that most powders and gels have a solubility of 100-130 ppm SiO_2, Iler (1979).

On the other hand, crystalline silica, such as quartz, almost universally present as "sand" has a much lower solubility, of the order of *6*ppm SiO_2. Supersaturated solutions of monomeric $Si(OH)_2$ are formed when silica is dissolved in water at high temperature under pressure and then cooled, or when an aqueous solution of soluble silicate is acidified:

$$Na_2SiO_3 + H_2O + 2HCI \rightleftharpoons Si(OH)_4 + 2NaCl \quad \text{.....(2.4)}$$

Supersaturated solutions of silicic acid in pure water are thermodynamically unstable because condensation polymerization through dehydration takes place. All higher polymers of whatever size, molecular weight, or state of hydration can be represented by a general formula containing *n* silicon atoms. The polymerization of additional monomer molecules or the deposition of silica can be represented as follows:

$$[Si_nO_{2n-\left(\frac{nx}{2}\right)}(OH)_{nx}] + m\,Si(OH)_4 \rightleftharpoons [Si_{n+m}O_{2n-\left(\frac{nx}{2}\right)+2m(2-p)}(OH)_{nx+4(m-p)}] + 2pm\,H_2O \quad \text{..... (2.5)}$$

Where *n* = number of silicon atoms in a polysilicic acid molecule or particle or polymeric network

x= number of OH groups per silicon atom in the polymer, not exceeding 4

m = the number of monomeric silicic acid molecules added to the polymer

p = fraction of the hydroxyl groups per monomeric silicic acid molecule that are converted to water during the polymerization reaction

Thus when *p* = 1, the monomer is converted to SO_2 within the polymer molecule without change in the number of OH groups in the polymer. There are, of course, restrictions such as *n* and *m* having to be integers and the values of x and *p* being limited by the possible structures of polymers and conditions of polymerization. However, for the case where dense amorphous silica is being deposited on extensive, massive silica surfaces from slightly supersaturated monomer solution, especially at high temperature and neutral or alkaline pH, x is very small, *p* is unity, and *n* is large. Thus the deposited silica may be essentially dense and anhydrous:

$$Si_nO_{2n} + m\,Si(OH)_{4)} \rightleftharpoons Si_{n+m}O_{2n+2m} + 2m\,H_2O \text{..... (2.6)}$$

Even vitreous or glassy silica contains some water, probably as SiOH groups. At a given temperature and humidity there is an equilibrium “solubility” of water in vitreous silica, according to Hetherington and Jack (1962). Flame-fused quartz contains 0.04 wt. % OH, whereas electrically fused material contains only 0.0003% as detected by infrared absorption at 2.73 micron wavelength. By extrapolation to30^0C, Moulson and Roberts (1960) concluded the equilibrium concentration of water in silica glass may be as high as 0.22% H_2O, probably present as internal SiOH groups.

Again, for the behavior of soluble silica in water, when the solution is highly supersaturated and insufficient solid silica surface is available to permit rapid deposition of soluble silica, new small nuclei particles are formed by inter condensation on monomer and low polymers. Silica is also deposited on these until supersaturation is relieved. It is in this manner that colloidal particles of silica are formed. These, in turn, may be aggregated to form silica gel or may be laid down as opal, both of which are highly porous with an extensive internal surface covered with SiOH groups. Thus "hydrated" silicas are formed. Very slow deposition may produce quartz, Iler (1979).

2.3 Soluble Silica-Monosilicic Acid

The soluble form of silica is monomeric, containing only one silicon atom and generally formulated as $Si(OH)_4$. This is often called monosilicic acid or orthosilicic acid. The state of hydration is not known, although at high pressure there is an indication that one water molecule is linked to each OH group, probably by hydrogen bonding. So the hydrated molecule is represented as $Si(OH : OH_2)_4$.The structure of monosilicic acid is assumed to involve silicon coordinated with four oxygen atoms as in amorphous vitreous silica and in crystalline quartz. Although there are rare minerals such as the stishovite form of SiO_2 or thaumasite, in which

silicon is coordinated with six oxygen atoms, silicon in most oxides and silicates is surrounded by only four oxygen atoms. If the monomer had the structure $H_2Si(OH)_6$, one would expect it to be a strong acid like the analogous H_2SiF_6, but in fact it is a very weak acid, Willey (1974).

It is essentially nonionic in neutral and weakly acidic solution and is not transported by electric current unless ionized in alkaline solution. It is not salted out of water nor can it be extracted by neutral organic solvents. It remains in the monomeric state for long periods in water at *25*°C, as long as the concentration is less than about 2×10^{-3} *M*, but polymerizes, usually rapidly, at higher concentrations, initially forming polysilicic acids of low molecular weight and then larger polymeric species recognizable as colloidal particles. The question often arises as to whether the term "soluble silica" should include the low polymers such as tetramer or decamer, which are classed as "oligomers." It becomes a matter of definition. "Soluble" materials have been recognized as those that pass through a dialysis membrane, whereas colloids do not; but even though membranes can now be made with pores sufficiently small to separate dextrose from sucrose, we think of sucrose as being "soluble." On the other hand, sucrose is certainly not colloidal.

Polysilicic acid is a polymer with molecular weights (as SiO_2) up to about 100,000, whether consisting of highly hydrated "active" silica or dense spherical particles less than about 50 Å in diameter. The arbitrary borderline of 50 Å or mol. wt. 100,000 is based on the general observation that below this point the polymer species are generally unstable, having only a transient existence owing to gelling or particle growth, it is below this size range that less than half of all the silicon atoms are present as SiO_2 that is, as ''silica," whereas more than half are each associated with at least one hydroxyl group. The term "silicic" acid is thus justifiable, Iler (1979). The preparation and reactions, for example, polymerization, of dilute solutions of

monosilicic acid are further described below. Meanwhile, some of its characteristics are noted, as follows, prior to discussing solubility:

I. It is characterized by rapid rate of reaction with molybdic acid to form the yellow silicomolybdic acid.

II. It is generally inert in neutral solution if the concentration is below the saturation level with respect to amorphous silica. Thus it is almost universally present at a concentration of a few parts per million in most natural waters and in living organisms.

III. It combines with metal ions to an increasing degree with increasing pH. Thus reducing the concentration of free monosilicic acid. (ferric and uranyl ions react at a pH as low as 2, whereas most other metal ions combine only at higher pH.)

IV. Above pH 9 it is ionized first to $(HO)_3SiO^-$ or at still higher pH to $(HO)_2SiO_2^{2-}$. The first equilibrium constant at 25°C is approximately (2.7, 2.8):

$$\frac{[(HO)_3SiO^-]}{[OH^-]\,[Si(OH)_4]} = 1.5 \times 10^4 \quad \text{.....(2.7) or}$$

$$\frac{[(HO)_3SiO^-]\,[H^+]}{[Si(OH)_4]} = 10^{-9.8} \quad \text{.....(2.8)}$$

Even though the silica solution is neutral, if it is passed through a bed of strong base cation exchange resin in the free-base form, the soluble silica in contact with the resin is ionized and is then held as silicate ions. In a mixture of Si(OH), in equilibrium with colloidal silica particles at pH 7-8, the particles bear a negative charge. According to Okamoto et al (1957) electrophoresis and transport studies show that the colloid, not the "molecularly soluble" $Si(OH)_4$, is the charge carrier. When the mixture is passed through a mixture of strong-base anion- and cation-exchange resin, monosilicic acid is removed, but not the colloidal particles. [After some time the particles dissolve sufficiently to reestablish the equilibrium concentration of $Si(OH)_4$.]

V. It is converted to H_2SiF_4 by reaction with HF in aqueous solution:

$$Si(OH)_4 + 6\ HF \rightleftharpoons 2\ H^+ + SiF_4^{2-} + 4\ H_2O \quad \ldots\ldots(2.9)$$

VI. It is converted *to* a complex anion by reaction with o-dihydroxy aromatic compounds. such as catechol, in neutral solution:

$$Si(OH)_4 + 3\ o\text{-}C_2H_4(OH)_2 + 2NH_4^+ + 2OH^- \rightleftharpoons (o\text{-}C_2H_4O_2)_3Si^{2-} + 2NH_4^+ + 8H_2O \ldots\ldots(2.10)$$

2.4 Phases of Silica

Since different phases of silica exhibit different solubility behavior, they are briefly described. By far the commonest crystalline form is quartz, the main constituent of common sand. However, under certain conditions in nature and in the laboratory, other forms are produced. These forms in turn may be divided into the following classes:

I. Anhydrous crystalline SiO_2.

II. Hydrated crystalline $SiO_2.xH_2O$.

III. Anhydrous amorphous silica of microporous *anisotropic* form such as fibers or sheets.

IV. Anhydrous and hydrous amorphous silica of colloidally subdivided or microporous *isotropic* form such as sols, gels, and fine powders.

V. Massive dense amorphous silica glass, Sosman (1965).

Of these, II, III, and IV exhibit extensive external or internal surfaces and are thus pertinent to the present study.

2.5 Polymerization of Silica

Graham et al (1995) made an intensive study of sols and gels, after that, many attempts have been made to explain the behavior of silicic acid. When freshly made by acidifying a soluble

silicate or hydrolyzing the ester, silicic acid is not "colloidal," since it diffuses easily through parchment or animal membranes and has a molecular weight by freezing point depression corresponding to monomer. Soon the molecular units become larger and pass through membranes only slowly and then not at all. This could be because the monomer or other small primary particles form aggregates, or because the individual particles increase in size and decrease in number.

A "micella" is a terminology used to defined colloidal particle in which foreign substances (ions, water) are present in its structure, that is, a porous aggregate, whereas the "amicron" is a discrete particle too small to be seen with the ultra-microscope. It was observed that such particles in a colloidal solution could "consist of one very large molecule," in other words, a single unit, not an aggregate.

Because the most obvious behavior of a silicic acid solution is that it increases in viscosity and finally forms a gel, its polymerization was generally assumed to be an aggregation process or a polymerization by which smaller molecular units linked together into larger ones. The nucleation and growth of discrete particles prior to the stage where aggregation begins have not been recognized by many workers, who held to the idea that $Si(OH)_4$ polymerized into siloxane chains which then were branched and cross-linked as in many organic polymers. Even now attempts are still made to apply the idea of monomer functionality and condensation polymerization theory of organic chemistry to the silica system. In fact, there is no relation or analogy between silicic acid polymerized in an aqueous system and condensation type organic polymers.

In 1925, Kruyt et al pointed out that there are two groups of silicic acid sols. The first group has a pH of 4.5 or less, and the viscosity of the sol increases with time. On the other hand, pure silica sols, having a pH of 7 or higher, are relatively stable, the viscosity either remaining the same or

decreasing with time. This difference in behavior is explained as follows. The more alkaline sols bear a negative charge and are thereby stabilized. However, the addition of soluble salts lowers the charge of the particles and causes gelation or flocculation. On the acid side, where there is essentially no charge, aggregation or flocculation occurs, causing an increase in viscosity, and eventually gelation.

Carman (1940) was the first to clearly state that silicic acid polymerizes to discrete particles which then aggregate into chains and networks. The formation of silica gel can be regarded as taking place in two stages. In the first, initially formed $Si(OH)_4$ condenses to form colloidal particles. In dilute solution, a further slow increase in particle size is the only subsequent change, but at a concentration of about one (1) percent silica, these primary particles are able to condense together to give a very open but continuous structure, extending throughout the medium, thus bestowing a certain degree of rigidity upon it. In both stages of polymerization, the mechanism is the same, that is, condensation to form Si-O-Si links, but in the first stage, condensation leads to particles of massive silica, while in the second, since it is not possible to fit two particles accurately together over a common face, the number of $Si-O-Si$ linkages between particles is fewer in number than those within the particles themselves. They are merely sufficient to bind adjacent particles together, in a fixed position relative to one another, and thereby lead to a rigid, highly porous, tangled network of branching chains. Thus three stages are actually recognized:

I. Polymerization of monomer to form particles.
II. Growth of particles.
III. Linking of particles together into branched chains, then networks, finally extending throughout the liquid medium, thickening it to a gel.

Since Carman published this in 1940, further experimental data continue to confirm his point of view. There is general agreement that polymerization, that is, the reactions that result in an increase in molecular weight of the silica, involves the condensation of silanol groups:

$$-SiOH + HOSi- \rightleftharpoons -SiOSi- + H_2O \quad \text{.....(2.11)}$$

The term "polymerization" is used in its broadest sense, the mutual condensation of Si(OH) to give molecularly coherent units of increasing size, whether these are spherical particles of increasing diameter or aggregates of an increasing number of constituent particles. Formation and growth of spherical particles is one kind of polymerization that takes place under certain conditions. Aggregation of particles to form viscous sols and gels is another kind of polymerization occurring under other conditions. Both types of polymerization may occur at once.

2.6 General Theory of Polymerization

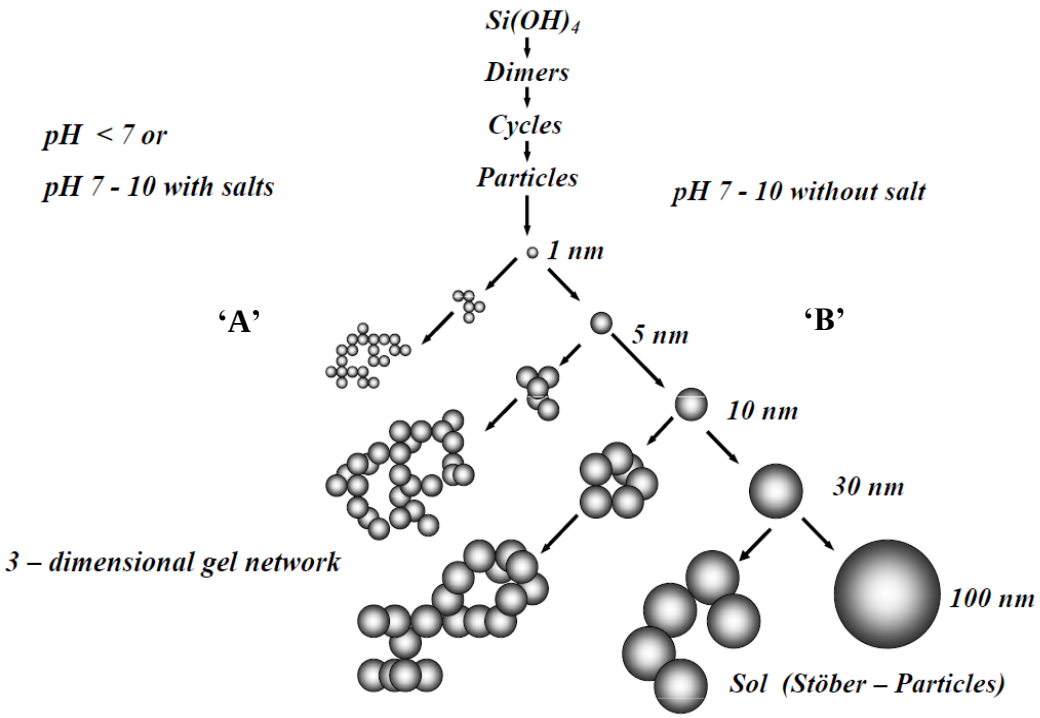


Figure 2.1: Polymerization behavior of silica. In basic solution *(B)* particles in sol grow in size with decrease in numbers: in acid solution or in presence of flocculating salts *(A)*, particles aggregate into three-dimensional networks and form gels. Brinker et al, 1990

Succeeding steps in polymerization from monomer to large particles and gels or powders have been represented schematically by Brinker et al (1990) as shown in Figure 2.1. This applies to aqueous systems, in which silica is somewhat soluble. Very little is known about the polymerization when $Si(OH)_4$ is formed in non-aqueous solutions. The individual steps are as follows:

(a) Monosilicic acid is soluble and stable in water at 25^oC for long periods of time if the concentration is less than about 100 ppm as SiO_2. When a solution of monomer, $Si(OH)_4$, is formed at a concentration greater than about 100-200 ppm as SO_2, that is, greater than the solubility of the solid phase of amorphous silica, and in the absence of solid phase on which the soluble silica might be deposited, then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid.

(b) The condensation polymerization involves an ionic mechanism. Above pH *2* the rate is proportional to the concentration of OH^- ion and below *2* to the H^+ ion.

(c) Silicic acid has a strong tendency to polymerize in such a way that in the polymer there is a maximum of siloxane (Si-O-Si) bonds and a minimum of uncondensed SiOH groups. Thus at the earliest stage of polymerization, condensation quickly leads to ring structures, for example, the cyclic tetramer, followed by addition of monomer to these and linking together of the cyclic polymers to larger three-dimensional molecules. These condense internally to the most compact state with SiOH groups remaining on the outside.

(d) The resulting spherical units are, in effect, the nuclei that develop into larger particles. The solubility of these very small particles depends on the particle size, that is, the radius of curvature of the surface. It also depends on the completeness of the dehydration of the internal solid phase.

If the latter is formed at ordinary temperature it may contain uncondensed OH groups but if formed above 80^0C, and especially above pH 7, it is almost anhydrous.

(e) Because small particles are more soluble than larger ones and since not all the small three-dimensional particles are the same size, the particles grow in average size and diminish in numbers as the smaller ones dissolve and the silica is deposited upon the larger ones. However, the higher solubility of smaller particles is pronounced only when the particle size is smaller than about *5* nm and very pronounced when it is less than 3 nm. Hence above pH 7, where the rate of dissolution and deposition of silica is high, particle growth continues at ordinary temperature until the particles are 5-10 nm in diameter, after which growth is slow. However, at low pH, where the rate of polymerization and de-polymerization is slower, particle growth becomes negligible after a size of 2-4 nm is reached. At higher temperatures, growth continues to larger sizes, especially above pH7.

The very early formation of particles was also proposed by Vysotskii et al (1973), who studied the early stages of polymerization and similarly stated that there are two basic processes of particle growth of silica in the aqueous system:

I. Growth of particles at the expense of silicic acid in the solution from the moment of its preparation.
II. Further growth of larger particles by deposition of silicic acid dissolving from the smaller particles. This is a slower process and may be negligible at low pH after the monomer has been used up.

(f) Above pH 6 or 7**,** and up to 10.5, where silica begins to dissolve as silicate, the silica particles are negatively charged and repel each other. Therefore they do not collide, so that particle growth continues without aggregation. However, if salt is present at a concentration greater than

0.2-0.3 *N*, as when sodium silicate is neutralized with acid, the charge repulsion is reduced and aggregation and gelling occur. It is paradoxical that under some conditions, precipitation or gelling is prevented by raising the temperature. In this pH range a sol of 2-3% silica with a borderline salt concentration of 0.2-0.3 *N* gels if aged at ordinary temperature. However, if the sol is first heated to 80-100^{0}C the particles grow in size and decrease in number so that aggregation and gelling are greatly retarded or even prevented permanently.

(g) At low pH the silica particles bear very little ionic charge and thus can collide and aggregate into chains and then gel networks. If the concentration of SiO_2 is more than 1% such aggregation may begin as soon as the first small particles are formed. However, at lower concentrations and at pH around 2, the monomer is converted largely to discrete particles before they begin to aggregate. On the other hand, at pH 5-6, monomer is converted rapidly to particles which simultaneously aggregate and gel so that it is not possible to separate two processes. The rate of aggregation increases rapidly with concentration so that in any case above 1% silica, aggregation probably involves not only particles but also oligomers, Iler (1979).

The process of aggregation and gelling in the silica system is unique because, unlike other metal oxides, the solid phase remains completely amorphous and appreciably soluble in water and is generally in solubility equilibrium with the monomer. It is essential to understand that while sol is being converted to gel, the growing aggregates contain the same concentration of silica and water as in the surrounding sol regions. These aggregates or "gel phase" cannot be seen because the density and refractive index of the gel phase are the same as those of the remaining sol. Thus before the sol solidifies only a slow increase in viscosity can be noted, with little change in other properties, up to a point where the viscosity begins to increase rapidly and solidification occurs at the "gel point." The most common way of determining the "gel point" is to observe when the meniscus of a sol in a container no longer remains horizontal when the container is tilted.

It may be difficult to visualize how particles in a suspension can rearrange themselves into three-dimensional networks without changing the silica concentration. In certain microscopic regions in the sol the particles arrange themselves in chains, and these in turn branch and form networks. These can be isolated in sols gelling at low pH by adding an inert miscible fluid such as water or alcohol. With a two-fold dilution, all the particles not attached to a three-dimensional network move apart. But the rigid networks retain their structure and thus are denser than the medium, and so can be separated by centrifuging. In this way the percentage of silica that has been converted to "gel phase" can be measured. Gelling occurs when about half of the silica has entered the gel phase, which can be thought of as spherical solidified regions in suspension which cause a rapid increase in viscosity when the "volume fraction" reaches about 0.5.After the gel network has been formed, the structure becomes stronger as the necks between particles become thicker owing to solution and deposition of silica.

2.6.1 Overall effect of pH on gelling

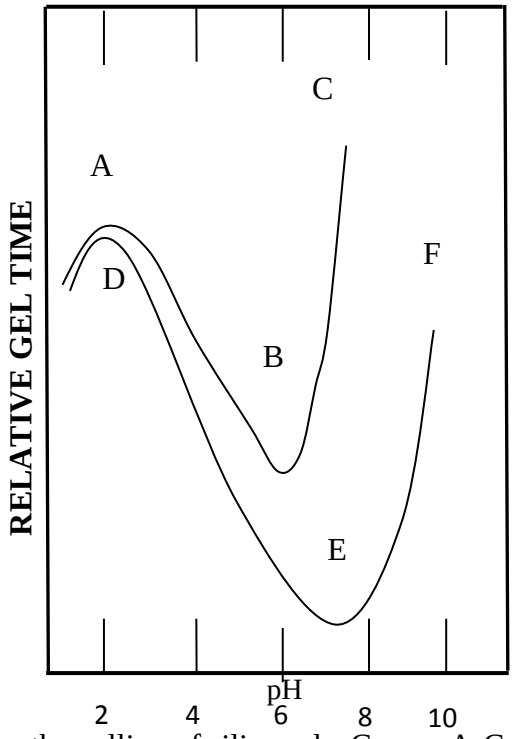


Figure 2.2: The effect of pH on the gelling of silica sols. Curves A-C-sols in the absence of sodium salts; *D-F:* in the presence of sodium salts. Iler, 1979.

Whether polysilicic acids or larger particles of colloidal silica are involved, the general effects of pH are generally as indicated schematically in Figure 2.2. Curve *ABC* represents the behavior of silica in the absence of salts. Sols have a maximum temporary stability with longest gel time around pH 1.5-3, and a minimum stability with rapid gelling around pH 5-6. Above about pH 7, no gel is formed since the particles are charged and only particle growth occurs. Curve *DEF* represents the general behavior when an electrolyte such as NaCl or Na_2SO_4 is present at a concentration above about 0.2-0.3 *N*. The salt lowers the ionic charge on particles. At low pH both sols gel, and salt has little effect. In the neutral region the pH of minimum stability is higher *(E)* when salt is present.

2.7 Monosilicic Acid

Monomeric silicic acid, $Si(OH)_4$ has never been isolated. It is a very weak acid and exists only in dilute aqueous solution, since it polymerizes when it is concentrated. It is the soluble form of silicathat is in equilibrium with the solid phases. It is a neutral highly hydrophilic, essentially nonionized substance that cannot be isolated from water. In pure form, if it could be prevented from polymerizing, it might be expected to be a clear liquid resembling glycerin. The basis for this speculation is that a very low molecular weight polysilicic acid was isolated as a clear viscous anhydrous liquid, it was found that it polymerized immediately to clear, hard silica gel when exposed to a trace of atmospheric moisture. It was highly hygroscopic, and soluble in polar organic solvents such as alcohol, but insoluble in hydrocarbons, Robinson (1946).

2.7.1 Preparation of monosilicic acid

A saturated solution of monosilicic acid, $Si(OH)_4$, containing about 0.01% SiO_2, is obtained when pure amorphous silica is equilibrated with water at room temperature. A more concentrated (supersaturated) solution can be obtained only indirectly by liberating monosilicic acid from its

compounds under carefully controlled conditions; at low temperature and low pH dilute solutions remain supersaturated with respect to amorphous silica for appreciable periods. For example, at pH3 and 0^0C, solutions of monosilicic acid up to 0.1 *M* (0.6% SiO_2) can be prepared by spontaneous hydrolysis of monomeric silicon compounds, such as silicon tetrachloride or methyl orthosilicate, and also by reacting monomeric silicates, such as sodium or magnesium orthosilicates or hydrated crystalline sodium metasilicate, with dilute acid.

2.7.2 Silica dissolution

Jander et al (1976) reported that amorphous silica gel gives a true solution of silica in water; it was later found that the silica in solution had a diffusion coefficient of $0.53m^2/s$, indicating a molecular size about equivalent to $Si(OH)_4$. Subsequently, Iler (1979) verified that amorphous silica exhibits a definite equilibrium solubility in water, amounting to about 0.01-0.012% SiO, in the saturated solution. Kitahara et al (1955) dissolved quartz under high pressure at 400^0C to obtain a solution containing 350-400 ppm which was quenched to obtain a solution of monomer at pH 6 which then polymerized. A 400 ppm solution of monomer was obtained by saturating water with silica gel at 95-100^0C. It was reports that in the pH range 1.2-3.7 it remains unpolymerized even after 2 hr. This appears to be a convenient way to make and store a 400 ppm solution of monomer for polymerization or deposition studies at 25^0C, where the solubility of gel is around 100-120 pprn.

2.8 Preparation Methods of Silica Sol

Hyung et al (2010) reported four typical routes to prepare colloidal silica from natural ore. The first among them is the preparation of colloidal silica from liquid sodium silicate by the ion exchange process. The sodium silicate is obtained from naturally available silica by melting the

silica ore in the presence of alkali flux; subsequently, it is dissolved by heating under pressure to produce liquid sodium silicate, which is commonly known as water glass.

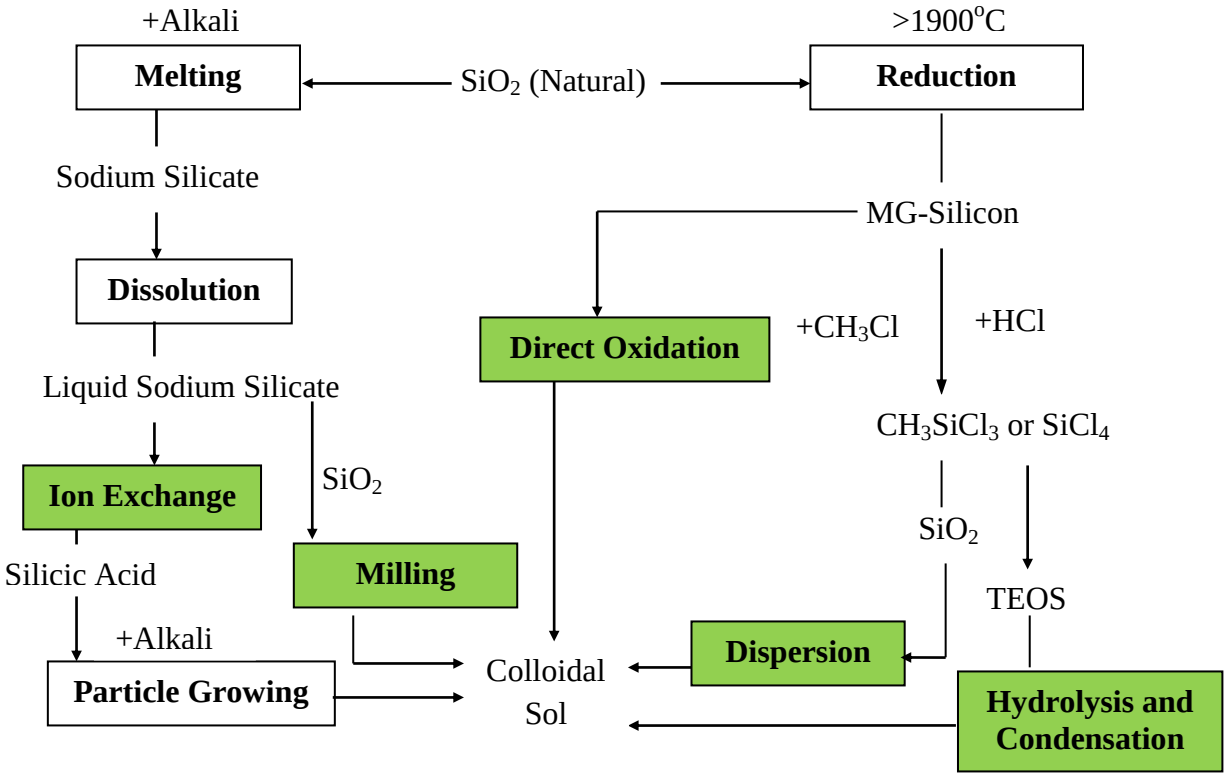


Figure 2.3: Preparation methods of silica sol. Hyung et al (2010)

The liquid sodium silicate has high viscosity, and therefore it is diluted to a concentration of 3-5 wt.%. Next, it is passed through an ion-exchange resin, and then fed into the alkali solution to form a silica seed, which is then used to grow silica particles. The product is concentrated to 30wt% to obtain the commercial product. The second method for preparing colloidal silica is from tetraethoxysilane (TEOS), which is well known as the Stöber method. TEOS is a silane monomer prepared from tetrachlorosilane, which in turn is derived from metallurgical-grade silicon. The silicon itself is obtained by the reduction of naturally occurring silica ore at temperature over 1900^0C in the presence of carbon. The third method is that of direct oxidation of silicon wherein colloidal silica is prepared by the direct oxidation of metallurgical grade

silicon without using TEOS. The silicon is treated with water in the presence of alkali catalysts to produce silica along with the evolution of hydrogen and heat. Finally, the fourth method for preparing colloidal silica is by milling and peptization of silica that can be found either in the form of silica gel or fumed silica, which consists of preferentially coaccervated or aggregated primary silica particles. The properties of the colloidal silica prepared by this route largely depend not only on the milling and peptization process but also on the properties of the starting silica source such as purity, shape, and aggregation. Colloidal silica is often defined by its solid content, counter ion type and concentration, pH, and particle size of silica.

Peptization method is one of the methods which was considered in this work. However, another method has been proposed in this research. In the new method, unlike in the peptization where hydrogel is dispersed to a sol by means of heating and stirring under non-evaporative condition, the hydrogel is dispersed to a silica sol by the aid of an ultra-sonicator (which is available in the department and that provide excellent dispersion of hydrogel and better stability in the sol) and the method is called an ultra-sonication method.

2.9 Previous Related Works

ZSM-5 (Zeolites Socony Mobil number five) is an aluminosilicate with high silica to alumina ratio (ten to several thousands) and has suitable properties for application in catalysis, adsorption and membrane science, Wilson et al (2014). At present, the main problem in zeolite research is the availability and cost of raw materials especially the silica. The benefits of using kaolin as an aluminosilicate source in zeolite synthesis are widely known. However, zeolites prepared from natural kaolin are always contaminated with trace amount of iron, titanium, calcium, magnesium, etc. which are originally present in the natural kaolin. These elements have influence on the quality of the zeolites, Dimitar et al (2009). Kaolin clay contains kaolinite with a SiO_2/Al_2O_3

molar ratio close to 2 and therefore it is well suited for the preparation of low-silica zeolites such as zeolite A, Sanhueza et al (1999). Preparation of zeolites with higher SiO_2/Al_2O_3 molar ratios such as zeolites X, Caballero et al.(2007), Colina and Lorens (2007) and Y, Atta et al (2007) from kaolinite has also been reported; Synthesis of zeolites with high SiO_2/Al_2O_3 molar ratio requires either an increase in the amount of silica or partial removal of alumina. Synthesis of ZSM-5 from kaolin with additional sources of silica has been reported, Khatamian and Irani (2009), Kovo et al (2009). In addition, ZSM-5 with high SiO_2/Al_2O_3 molar ratio using dealumination method, Wilson et al (2014), and metakaolin and silica sol, Feng et al (2009) have also been synthesized. As the major component, silica is frequently employed inform of a sol during the synthesis of ZSM-5, the sol is normally produced from a monomeric silicates source (usually sodium silicate). Casimer et al (1955) prepared silicic acid sol by neutralization reaction at pH above 7, forming a silica hydrogel; the hydrogel was washed and peptized to silicic acid sol under non-evaporative condition. Mahulikar et al (2006) produced colloidal silica by dissolving fumed silica in an aqueous solvent having an alkali metal hydroxide via ion exchange method. Adjusting the pH, temperature and silicic acid concentration gave sol having a mean particle size of about 2 nm to 100 nm. Chul-Joo et al (2008) study the kinetics of sodium silicate solution and the condensation between silicic acid species and silica nuclei surfaces at 20-80^oC. It was observed that the overall condensation is first order in silicic acid species concentration. Sodium silicate solutions having a variety of concentrations were passed through ion exchange resin to prepare the silicic acid solutions, Karami et al (2008). It was discovered that particle size and surface area of prepared silica sol are influenced by formation temperature, titration rate, silicic acid and alkaline solutions concentration. It was clear that none of the previous works reported silica sol preparation from kaolin and the ones prepared from other silica sources were not used for ZSM-5 synthesis. In addition, all the reports on ZSM-5 synthesized from kaolin had

SiO_2/Al_2O_3 molar ratio below 40 which indicates low catalytic activities and poor thermal stability, and relatively high amount of trace contaminants compared to the zeolites synthesized using high purity chemical precursors. The aim of the present work is to utilize kaolin as a silica source (by producing sodium silicate and silica sol from it) for the synthesis of high purity ZSM-5 using complete dealumination method, which enhances its economic competitiveness.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials/Reagents

Kankara clay from Kankara L.G.A., Katsina State used as the silica source (raw material). Deionized water and distilled water (from PTDF Chair laboratory), used for solution preparation and samples washing. Sodium hydroxide (Sigma Aldrich, reagent grade, 98%, anhydrous pellets), used for sodium silicate preparation and also saved as the mineralizing agent during ZSM-5 synthesis. Conc. sulfuric acid H_2SO_4 (98%, Sigma Aldrich) was used for dealumination, silica sol preparation and during the zeolite synthesis. Barium chloride (Echas) was used for testing the presence of SO_4^{2-} ions during washing of the silica sol. Stainless steel sheets (SS 304), 2mm thick, pipes and fittings use for the fabrication of sodium silicate pilot plant. Teflon rod, 100mm thick used as a pipe in the heating portion of the pilot plant.

2.2 Apparatus

Some of the apparatus used in this work include among others, laboratory mortar and pestle (ceramic), tyler mesh sieve (70µm), buchner flask (1 liter), sintered glass filter funnel (quickfit TM), ceramic pot, desiccators (dry seal type, jencons), plastic sample containers and propylene bottles (150ml).

3.3 Equipment

Table 3.1: List of equipment

S/N	Name	Model	Manufacturer
1	Weighing scale (0-100kg Range)	1455T 18	WEDA, Holland
2	Oven(0-260^{0}C)	TM OV-420	Gallenkamp, England
3	Analytical balance	AB 204 (0-180g)	MettlerToledo, Switzerland
4	Vibrator	ZW (0.75) kW	
5	High vacuum pump	ES-100	Edwards, England

6	Electric furnace (0-1400^{0}C)	TIKIR 11/12	Heraeus, Holland
7	Band heater with temperature control 600W (220V) 4cm diameter		
8	Distiller	A4000	Aquatron
9	X-ray fluorescence machine	Minipal 4	PANalytical, Holland
10	X-ray diffractometer	Empyreal	PANalytical, Holland
11	Ultra-sonicator	350	HS-U, INC., New York
12	Plastic pump	W-350-B	
13	Magnetic Stirrer	78HW/AMS300	

3.4 Methodology

3.4.1 Dealumination of meta-kaolin

Dealumination of meta-kaolin (beneficiated Kankara kaolin that was activated for 2hrs at 750^{0}C) was done according to the procedure reported by Ajayi et al (2006). However, attempt was made to reduce the initial quantity of acid used for the dealumination and further introducing second dealumination.

3.4.2 Preparation of sodium silicate

Twenty grams (20g) of silica were dissolved in NaOH solution and placed in a propylene bottle followed by heating and stirring on a magnetic stirrer for 1 to 3hrs. The resulting mixture was allowed to cool to room temperature and then filtered. Hot deionized water at 100^{0}C was used to wash the residue.

3.4.3 Preparation of silica sol

About 200 ml of sodium silicate solution obtained in stage two (3.4.2) was titrated with 1 M solution of H_2SO_4 with constant stirring and heating at 50^{0}C on magnetic stirrer until pH > 7 for basic silica sol, pH = 7 for neutral silica sol and a pH < 7 for acidic silica sol. A cloudy, viscous gel was formed, and the gel was allowed to cool to room temperature. When sodium silicate was

acidified, a supersaturated solution of silicic acid, $Si(OH)_4$ monomers was formed, as described by Equation (3.1).

$$Na_2O{\bullet}3SiO_2 + H_2SO_4 \longrightarrow 3SiO_2 + Na_2SO_4 + H_2O \quad \text{..... (3.1)}$$

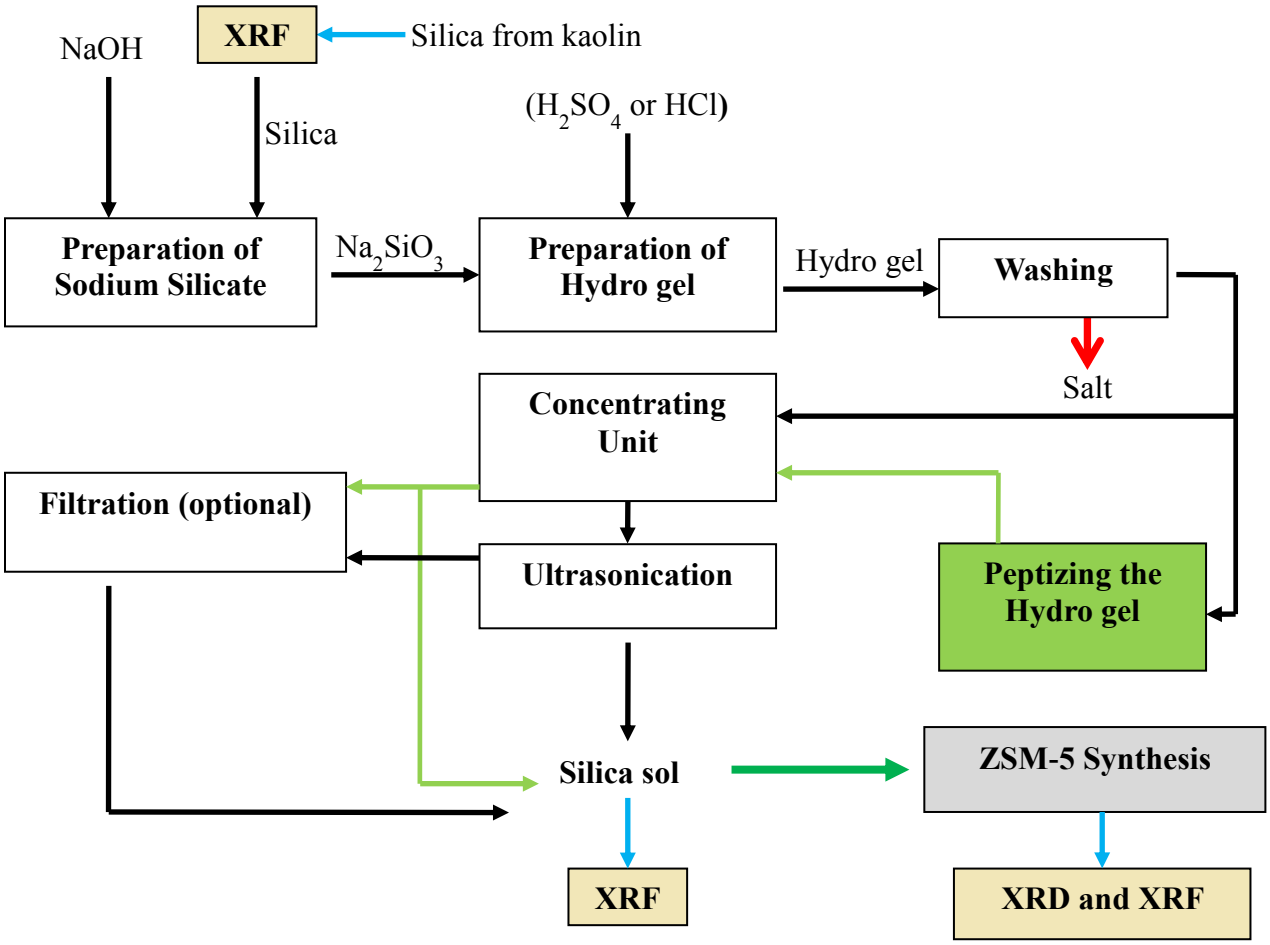


Figure 3.1: Block Diagram of the Silica Sol Preparation by Peptization and Ultrasonication

The gel was washed repeatedly with hot de-ionized water. Diluted barium chloride solution was added to the filtrate for testing the removal of SO_4^{2-} ions. Its presence was indicated by the formation of a white precipitate. This test was repeated until no white precipitate was formed on addition of barium chloride. Gel washing with water removes trapped sodium sulphate (Na_2SO_4) in the pores of the gel network. The gel formed was then concentrated to a volume of 25 ml by allowing it in a 250 ml polypropylene bottle and then placed in oven at 100^0C for 24hrs. The

concentrated gel was then dispersed using an utrasonicator (cell distruptor) to give a desired silica-sol. For peptization method the hydrogel was dispersed first by heating under non-evaporative condition with constant stirring for two hours before concentrating the sol. The silica sol obtained was then used to synthesize ZSM-5 using the hydrothermal procedure as reported by Lisensky et al (2010) and the samples were analyzed using XRD and XRF respectively.

3.4.4 Design methodology

The idea was the design of variation of the conventional packed bed reactor. The immobilized catalyst bed was replaced with silica sand, as this would minimize the movement of the silica and adequately address the erosion corrosion problem. The difference from the conventional packed bed reactor was that instead of having the caustic solution pass once through the sand bed it was re-circulated continuously until the silica was dissolved. The design consists of two main componets: a packed bed reactor and a holding tank. The holding tank functions were to store re-circulating 50% caustic solution as well as to collect the sodium silicate product. Other units (pump, piping, heating and control) were carefully selected to suite the objective of this work. The piping system (including the pump) was used to transport the fluids from the holding tank to the top of the reactor while the heating and control system was used to achieved and maintain the required temperature until the process was completed.

3.4.5 Design of the reactor

A schematic diagram of a packed bed reactor is shown in Figure 3.2. Mass balance of the system was determined using the stoichiometry of the reaction between the silica and the sodium hydroxide as shown in equation 3.2.

$$2NaOH + xSiO_2 + H_2O \longrightarrow Na_2O(SiO_2)_x + 2H_2O \quad \text{.................................(3.2)}$$

The *x* in the equation represents the different grade of the sodium silicate which can be produced from the reaction. The silica to sodium hydroxide ratio (mass ratio) used was based on most of the zeolite grade sodium silicate which was 2.4. Since this value was given in mass fraction, it was converted to a mole fraction of 2.5. The value was used to balance the coefficient of the equation, yielding equation (3.3).

$$2NaOH + 2.5SiO_2 + H_2O \longrightarrow Na_2O(SiO_2)_{2.5} + 2H_2O \quad \text{.....(3.3)}$$

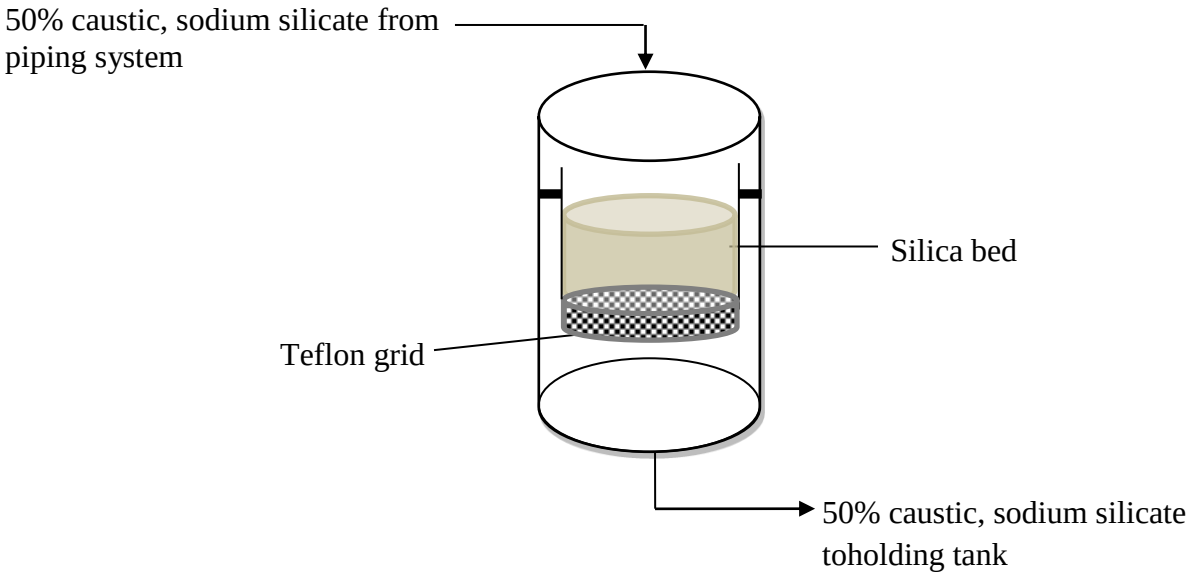


Figure 3.2: Packed bed reactor

Basis of 5000g silica input was chosen, based on this mass of the starting raw material, volume of the silica was determined. However, for a liquid fixed bed reactor Ulrich (2004) provided range of values for characteristic bed diameter and height. Ulrich also gave a list of characteristic superficial velocity for same type of reactor. Based on these available data and the objective of this work a bed diameter and bed height are selected. The total reactor height was then found by allowing for a head space of 1.5 times the height of the silica bed. The reactor height was also subjected to the constrains of the material available. A Teflon grid with 1mm pore size was placed at the bottom of the silica bed to support the bed and as well to prevent bulk of the silica

from proceeding into the holding tank. Based on the physical properties of the silica and the allowance given between the silica bed and wall of the reactor, pressure drop across the bed was negligible and therefore not considered.

3.4.6 Design of holding tank

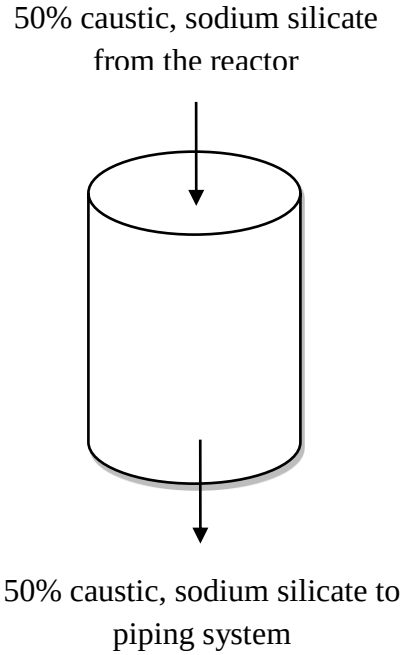


Figure 3.3: Caustic, sodium silicate holding tank

Holding tank was designed to take care of the second raw material which was the sodium hydroxide solution and also hold the sodium silicate product. From the stoichiometric equation (equation 3.3) of the overall reaction, the total mass of sodium silicate output was calculated from which the volume of the tank was determined. It was then decided to add a factor of 100% into the sizing in order to ensure safe operation.

3.4.7 Specification of other components

The following components of the sodium silicate production pilot plan were specified to suit the objective of the work;

i. Piping system (including pump)
ii. Heating system (with control)
iii. Vibrator and
iv. Flow meter

3.4.8 Fabrication procedure

After determining the necessary dimensions and specifying other units, the steps followed during the fabrication of the pilot plant are shown below:

i. Production of the process flow diagram
ii. Details drawing of the pilot plant
iii. Purchase of materials
iv. Fabrication of the plant (at HANIGHA Nigeria, Kakuri Kaduna State)

The pilot plant was then coupled and test-run.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter presents the results of the various experiments conducted on treated Kankara kaolin to produce zeolite grade sodium silicate and silica sol. These include the results of the samples characterization using a range of techniques including X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). In addition, the kinetics of silica (from Kankara kaolin) dissolution in sodium hydroxide solution studied are presented.

4.1 Dealumination of Meta-Kaolin

4.1.1 Chemical compositions of silica

The summary of the chemical compositions using X-ray Fluorescence (XRF) carried out on the silica obtained from single dealumination of metakaolin with 4 and 2.5 folds acid, and double dealumination with 2.5/2.5, 2.5/3, 4/2.5 and 4/3 folds of acid respectively; is shown in Table 4.1. The results showed that, the single dealumination samples were rich of silica, 93.17%, and 94.34% with traces of alumina indicating incomplete dealumination. However, appreciable amount of iron, potassium, calcium, magnesium and titanium which are believed to affect the quality of the silica, hence the sodium silicate and the sol was noted. For the double dealumination it was observed that no alumina (Al_2O_3) was left after the second treatment in all the folds considered, which is an indication of complete dealumination. The percentage CaO was comparatively the same in the samples with double dealumination and relatively low compared to that from single dealumination. Low amount of K_2O and Fe_2O_3 were also recorded in the double dealumination, specifically the one with 4 fold initial whereas the one with 2.5 fold initial dealumination shows almost equal amount. However, regular trend was not observed for TiO.

Table 4.1: Chemical composition of silica obtained from dealumination of meta-kaolin

Oxides (wt%)	4 Fold SD	2.5 Fold SD	2.5/2.5 Fold DD	2.5/3 Fold DD	4/2.5 Fold DD	4/3 Fold DD
SiO_2	93.170	94.340	94.290	95.110	94.320	95.150
Al_2O_3	0.100	0.200	ND	ND	ND	ND
CaO	1.380	1.000	0.910	0.959	0.968	0.957
K_2O	1.740	1.670	1.680	1.700	1.410	1.450
Fe_2O_3	0.940	0.895	0.852	0.869	0.563	0.567
CuO	0.019	0.018	0.018	0.022	0.017	0.016
Cr_2O_3	ND	0.027	ND	0.031	ND	ND
TiO_2	0.150	0.160	0.16	0.210	0.250	0.260

4.2 Sodium Silicate and Silica Sol Preparation from Silica Obtained from Kankara Kaolin

4.2.1 Production of sodium silicate

The various concentrations of sodium hydroxide (NaOH) employed to produce the sodium silicate that was used in the preparation of the silica sols is presents in Table 4.2. Sodium hydroxide solutions of 0.8M and 1.5M gave percentage dissolutions of 16% and 26% respectively under heating at 90^oC and constant stirring for 2 hours. Appreciable condensation of silica was not observed when the resulting sodium silicate was reacted with mineral acid to produce the hydrogel, which was attributed to the dilute nature of the two sodium silicate solutions.

Nevertheless, when concentrations of 2.5M and 3.0M NaOH were used better dissolution of 77 percent and 78 percent were recorded under the same conditions of heating and stirring. The silica condensation was apparent when the sodium silicate obtained was reacted with acid and the hydrogel formed was strong. This was attributd to the relative concentration of the silica in the sodium silicate, which led to a stable and concentrated sol as shown by Karami et al (2008) that alkali solution concentration and the formation temperature are important factors not only on

particle growth but also for the stability of colloidal silica. Although 6.0M concentration of NaOH showed the highest degree of silica dissolution (95%) that gave a very strong hydrogel, unstable silica sol was obtained from it.

Table 4.2: The various concentrations of NaOH used in producing the sodium silicate at 90^0C for 1hr stirring time

S/N	NaOHConc. (mol/dm^3)	Dissolution (%)	Nature of the Sol
1	0.8	16	Very dilute
2	1.5	26	Dilute
3	2.5	77	Conc. and stable
4	3.0	78	Conc. and stable
5	6.0	95	Highly conc. and unstable

4.2.2 Preparation of silica sol

The nature of the three types of silica sols produced (acidic, basic, and neutral) by peptization method is shown in Table 4.3. They all displayed a good level of stability as they retained their colloidal form for two weeks (although some of the acidic silica sol aggregated later), the basic sol showed better stability (there was no aggregation and viscosity reduction was noticed).

Table 4.3: Types of silica sol produced by peptization method

S/N	Silica Sol	pH	Stability	Testing for ZSM-5 Preparation
1	Acidic	2.5-4	Stable	No formation
2	Neutral	7	Stable	No formation
3	Basic	9.5-11	Stable	No formation

On testing for zeolite preparation the three sols appeared to be unstable, as after combining all the ingredients, the resulting mixture could not retain its gel-like nature long enough before settling. The sols tested settled either immediately or did not crystallized at all and no formation of ZSM-5 was observed. For that reason they were considered not-stable for the purpose of ZSM-5 synthesis.

Table 4.4 presents the nature of the silica sol produced by ultra-sonication method. Like the peptization, this method gave a stable silica sol in the three pH regimes with the basic sol having superior qualities. It was however observed that the sols were not as translucent as the ones obtained from peptization method and had better stability when compared, testifying very good dispersion.

Table 4.4: Types of silica sol produced by ultra-sonication method

S/N	Silica Sol	pH	Stability	Testing for ZSM-5 Preparation
1	Acidic	2.5-4	Stable	No formation
2	Neutral	7	Stable	No formation
3	Basic	9.5-11	Stable	ZSM-5 formed

The silica sol prepared by ultra-sonication method stayed for more than three months without showing any sign of settling.

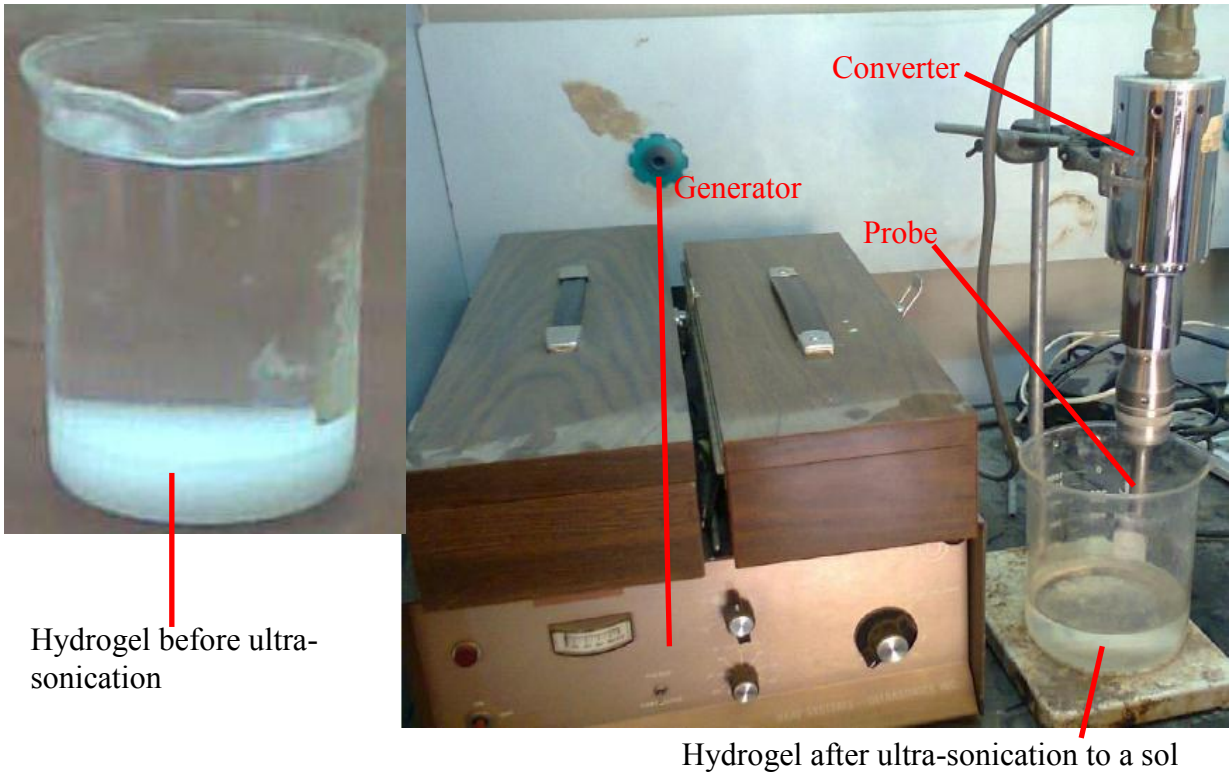


Plate 4.1: Ultra-sonicator set

However, only the basic sol provided the needed outcome on testing for zeolite synthesis. Though some of the sols neither settled instantly nor crystallized after the expected period of time, no formation of ZSM-5 were observed in both cases.

The extent to which the basic silica sol produced in this research via ultra-sonication method can be concentrated without compromising the issue of stability, in addition, producing ZSM-5 on testing is presented in Table 4.5.

Table 4.5: Concentration-stability of produced silica sol

S/N	Volume of Na_2OSiO_2 (ml)	Volume of Sol (ml)	Stability	Testing for ZSM-5 Preparation
1	200	25	Stable	No formation
2	400	25	Stable	ZSM-5 formed
3	700	25	Unstable	No formation
4	1000	25	Unstable	No formation
5	2000	25	Unstable	Not tested

Zeolite grade silica sols are mostly produced from high technology processes with silica contains ranging from 20 to 50%wt. Research and development, China Silicon Industry, 2010. Here, initial volume of 200, 400, 700, 1000 and 2000ml of sodium silicate were neutralized to produce the hydro gel which was washed, dispersed using ultra-sonicator, and concentrated to a final volume of 25ml. Both 200ml and 400 gave stable silica sols with 6-14 and 15-20 wt.% silica contain respectively, On testing for zeolite synthesis, only 400ml gave the required result but 200ml crystallized prematurely without ZSM-5 formation, as such 200ml was considered unstable. All attempt made to prepare sols with higher silica contain failed as increase in the amount of hydrogel only yielded unstable silica sols.

4.2.3 Chemical compositions of silica sol

Table 4.6: Comparison of the chemical compositions of commercial silica sol with silica sol from Kankara kaolin

Oxides (%wt.)	Commercial Silica Sol (Zeolite Grade)	Silica Sol from Kankara Kaolin SD	Silica Sol from Kankara Kaolin DD
SiO_2	99.23	99.27	99.50
Na_2O	0.01	0.006	0.007
CaO	0.15	0.24	0.22
K_2O	0.047	0.02	0.02
Fe_2O_3	0.338	0.0891	0.0824
CuO	0.012	0.012	0.013
SO_3	0.09	0.28	0.00
Cl	0.03	0.00	0.00
Ti_2O_3	0.021	0.00	0.00

Chemical compositions of the commercial zeolite grade silica sol and silica sol from single and double dealuminated Kankara kaolin is presents in Table 4.6 to enable comparison. It was observed that, silica was the dominant component in all the three samples, with the sol from single and double dealumination and that from commercial high purity chemical having percentage silica of 99.27, 99.50 and 99.23, respectively.

Moreover, the results showed the percentages of other compounds often associated with silica sol such as CaO, K_2O, Fe_2O_3, and Ti_2O_3among others, which are mostly referred to as impurities, the level of which depend on the silica source. Silica from clay had higher amount of such impurities as reported by Dimitar G. et al (2009), and that made it difficult to be used for zeolite grade silica source as these impurities influenced the quality of the zeolite produced. However, with the method adopted in this work, silica sol with less K_2O, Ti_2O_3 and very low Fe_2O_3 contents was produced. Although, percentage CaO was a bit higher in the prepared sol, but the chemical compositions of the two sols were very much similar.

The effectiveness of the method was also proven when the results in Table 4.1 were compared to those in Table 4.6. For single dealumination, the silica content of the raw silica sample was 94.34% but that of the prepared sol was 99.27%, whereas an increase in silica content from 94.29% in the raw silica sample to 99.50% in the produced silica sol was recorded for the double dealumination. There was noticeable reduction in the percentage content of CaO, K_2O, FeO_3 and Ti_2O_3 from 1.00, 1.67, 0.895 and 0.16 in the raw silica to 0.24, 0.02, 0.089 and 0.0 in the final silica sol for single dealumination, and for double dealumination, from 0.91, 1.68, 0.852 and 0.16 in the raw silica to 0.22, 0.02, 0.0824 and 0.0 in the final silica sol.

4.3 Powder Na-ZSM-5 Zeolites

4.3.1 XRD analysis of ZSM-5

Na-ZSM-5 samples were prepared using the commercial zeolite grade silica sol and the silica sol obtained from Kankara kaolin. The ZSM-5 samples obtained were examined using XRD and the patterns presented in Figures 4.4 and 4.5. The powder X-ray diffraction patterns were recorded over 2Ɵ range of 3^o to 50^o and the data were compared with those for simulated, standard and the commercial Na-ZSM-5(Figures 4.1, 4.2 and 4.3 respectively).

The XRD patterns of the prepared Na-ZSM-5 from Kankara kaolin and the commercial silica sol exhibited all the prominent peaks associated to ZSM-5 (peaks occurring at 7^o to 10^o, 13^o to 16^o, 23^o to 25^o, 29^o to 31^o and 45^o to 47^o) and the difractograms showed no noticeable difference from the sharpness of the peaks of Na-ZSM-5 in both the standard and the commercial XRD (see Figure 4.6). In addition, the purity of the zeolite samples as well as the absence of amorphous matter within the pore structures was confirmed.

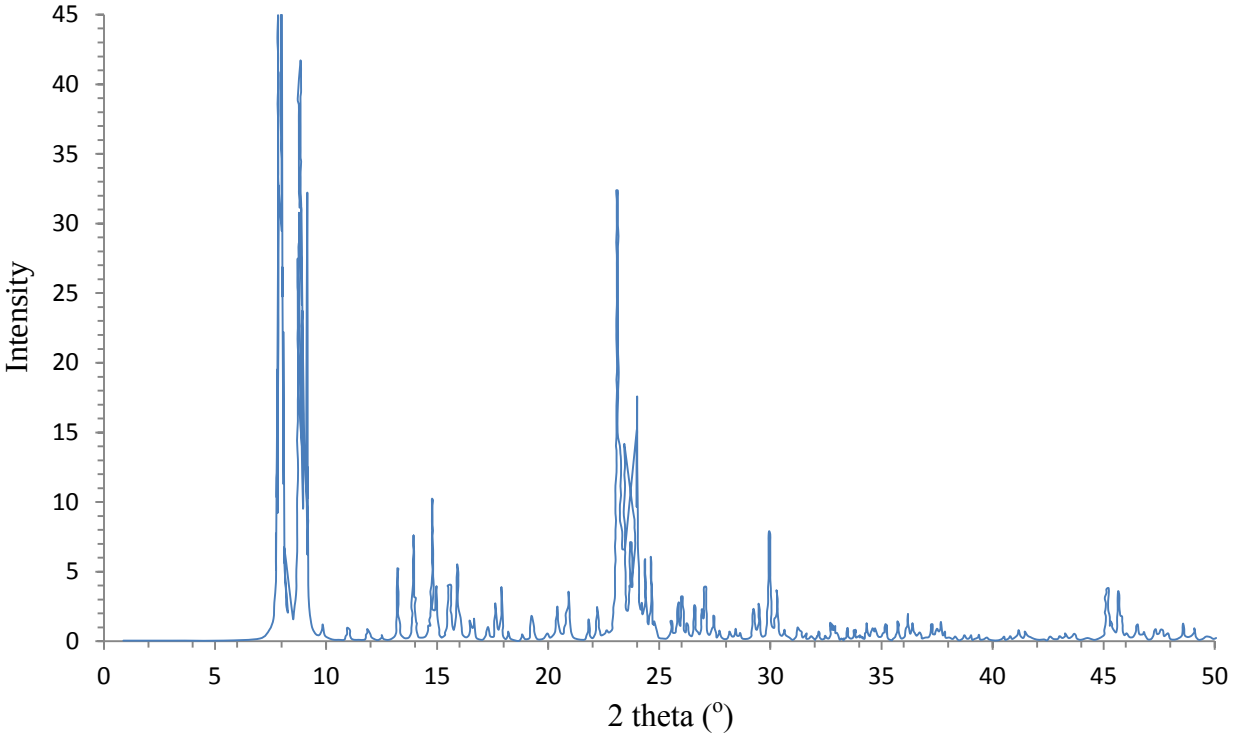


Figure 4.1: Simulated XRD pattern for Na-ZSM-5, Treacy et al, 2001.

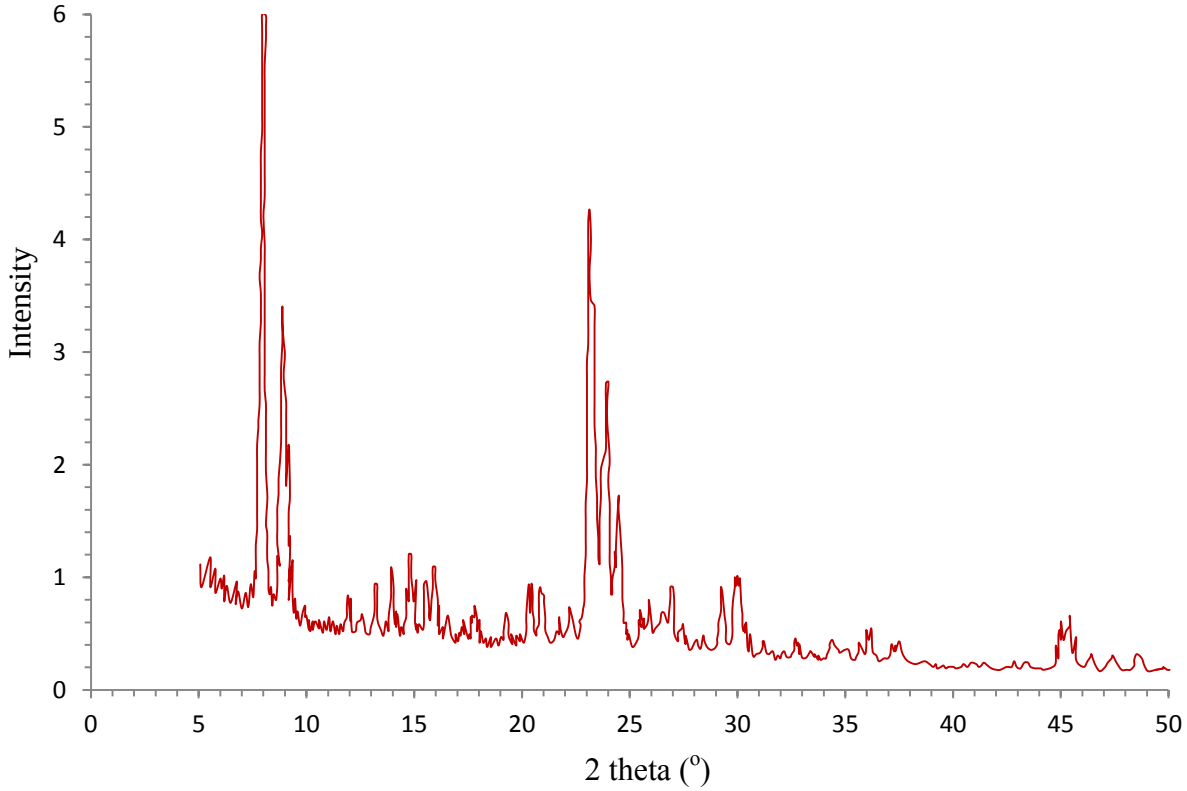


Figure 4.2: XRD patterns of the Standard Na-ZSM-5, Rana, 2013.

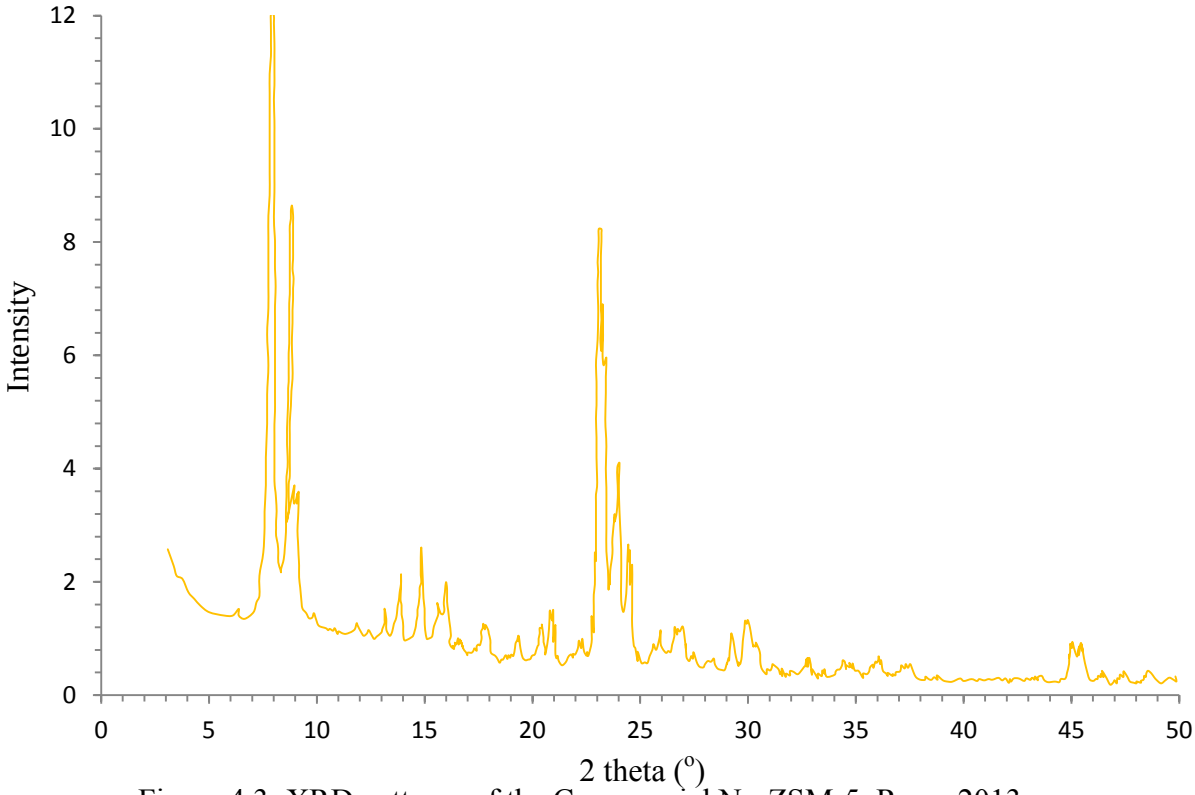


Figure 4.3: XRD patterns of the Commercial Na-ZSM-5, Rana, 2013.

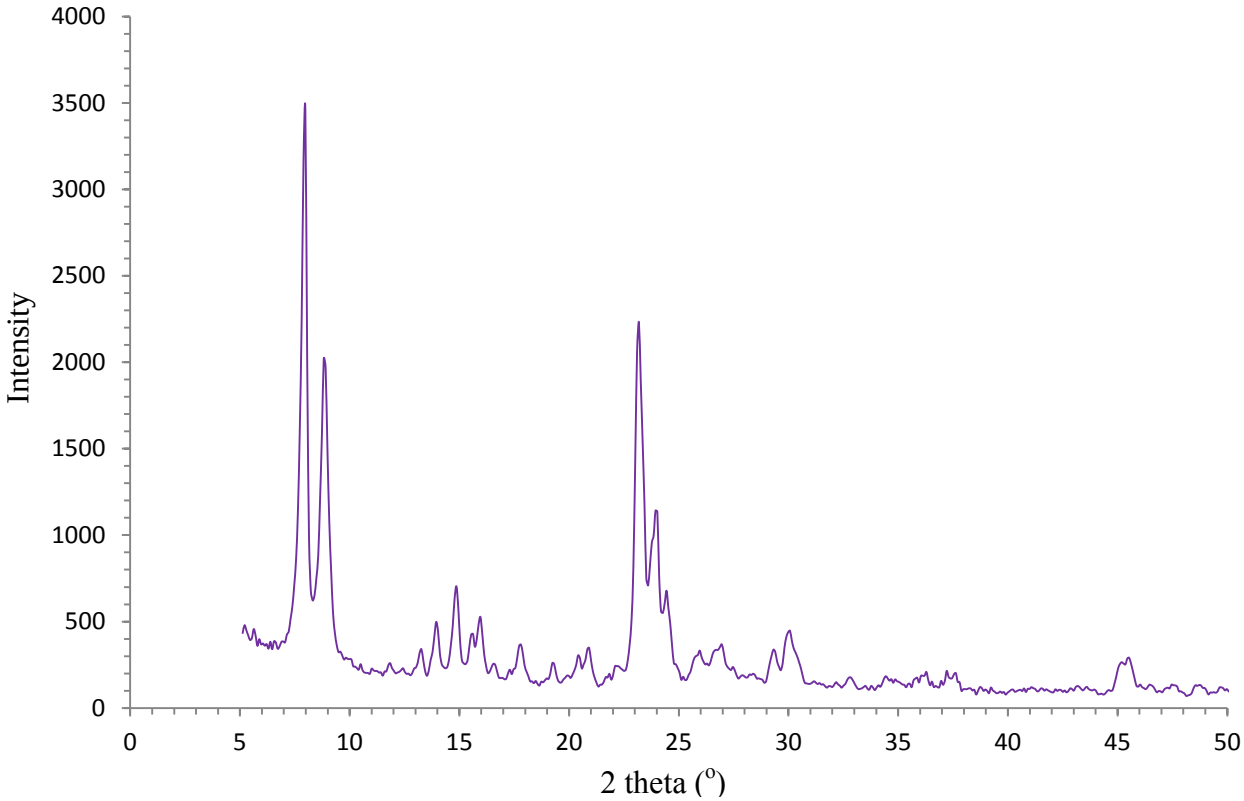


Figure 4.4: XRD pattern for Na-ZSM-5 synthesized from commercial silica sol

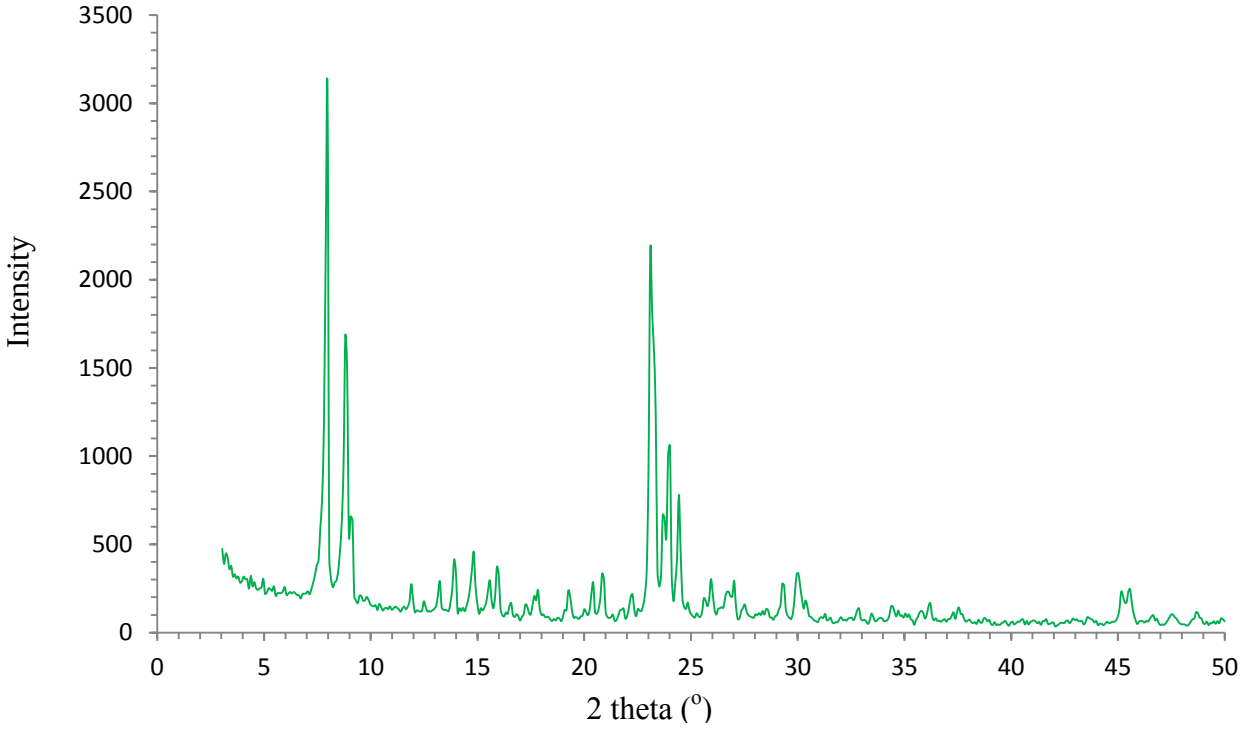


Fig.4.5: XRD pattern for Na-ZSM-5 synthesized from Kankara kaolin

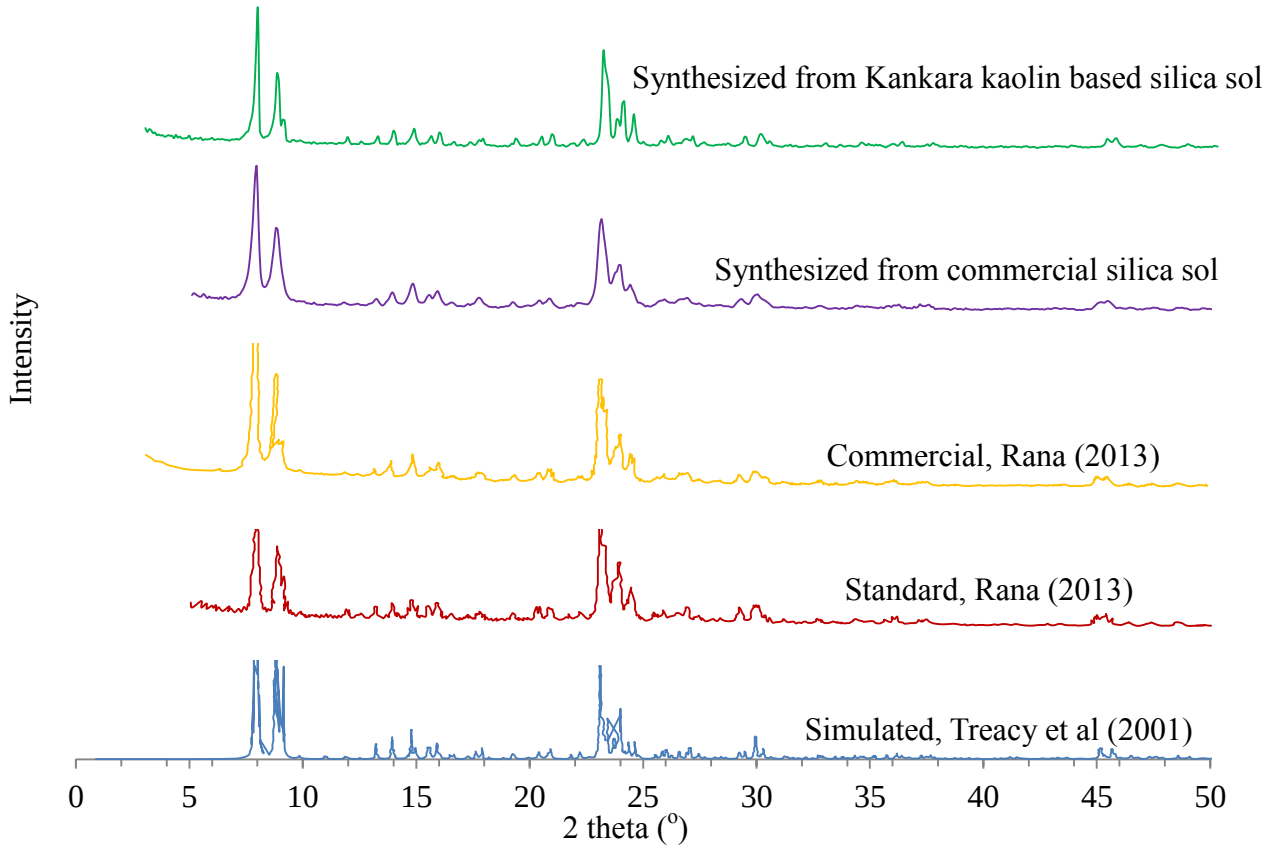


Figure 4.6: Comparison of the XRD patterns of Na-ZSM-5

4.3.2 XRF analysis of ZSM-5

The X-ray fluorescence results of the prepared Na-ZSM-5 characterization in comparison with Na-ZSM-5 from commercial silica sol are presented in Table 4.7. According to Raul F. L (2003) it is possible to prepare ZSM-5 with silica to alumina ratio (Si/Al) from about 8 to ∞. In this regard, the XRF confirmed that the products from both the commercial and the Kankara kaolin based silica sols were Na-ZSM-5. Though, the former was more siliceous, the later was purer and both fell within the class of high silica zeolites (Si/Al ≥ 10, Sushama M. K., 2002).

Table 4.7: Comparison of the chemical compositions of Na-ZSM-5 from commercial silica sol and silica sol from Kankara kaolin

Oxides (wt%)	**Na-ZSM-5 from Commercial Silica Sol**	**Na-ZSM-5 from Kaolin Based Silica Sol**
SiO_2	97.20	98.060
Al_2O_3	0.500	1.270
CaO	0.255	0.015
TiO_2	0.025	0.019
Fe_2O_3	0.114	0.065
MgO	0.020	0.150
CuO	0.255	0.015
SiO_2/Al_2O_3	**194.4**	**77.2**

Dimitar et al (2009) attributed zeolites prepared from kaolin as always contaminated with trace amount of iron, titanium, calcium, magnesium etc. which were originally present in the natural kaolin. It was evident from the results of this work that, when proper routes were followed, zeolites with equal or even better qualities could be produced from kaolin.

4.4 Design of Sodium Silicate Pilot Plant

4.4.1 Kinetics of silica dissolution in sodium hydroxide

Using the experimental data enabled the determination of both the reaction order and the rate constant by the integral method. Since sodium hydroxide was used in excess during the reaction,

the reaction rate was assumed to be largely dependent on the concentration of silica from Kankara kaolin. Thus;

$$2NaOH + SiO_2 + H_2O \longrightarrow Na_2O\,(SiO_2) + 2\,H_2O \quad \ldots\ldots\ldots\ldots (4.1)$$

$$X = \frac{CAo - CA}{CAo} \quad \ldots\ldots\ldots\ldots (4.2)$$

Table 4.8: Kinetic Data of Silica Dissolution

S/N	Time (min)	C_A (mol/dm^3)	X (%)
1	0.0	0.9487	0
2	0.5	0.6731	29
3	1.0	0.4997	47
4	1.5	0.4169	56
5	2.0	0.3247	66
6	3.0	0.2908	70

Using the integral method for a first order reaction the rate constant (*k*) can be determined fromthe slope of In (C_{Ao}/C_A) *vs* Time plot, so long as the line is linear.

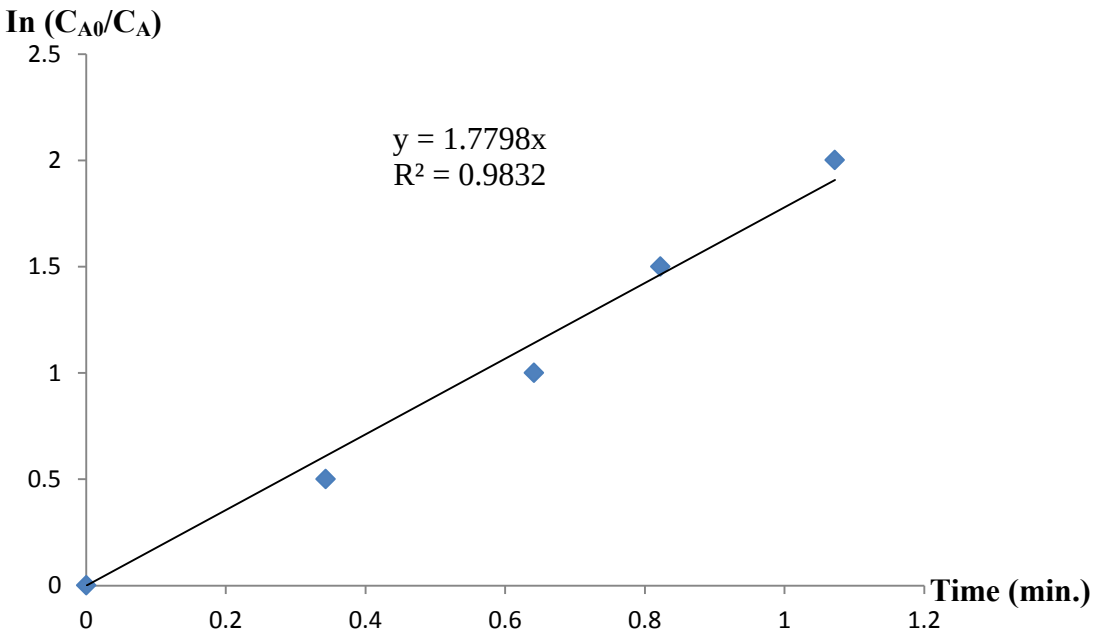


Figure 4.7: Rate constant and reaction order determination by integral method

From Figure 4.7

Rate constant = 1.7798min^{-1}

Reaction order = 1

4.4.2 Effect of temperature on silica dissolution

From the kinetics study of dissolution of amorphous silica from Kankara kaolin in sodium hydroxide solution, first order reaction law was found to describe the reaction with rate constant of1.7798/min.

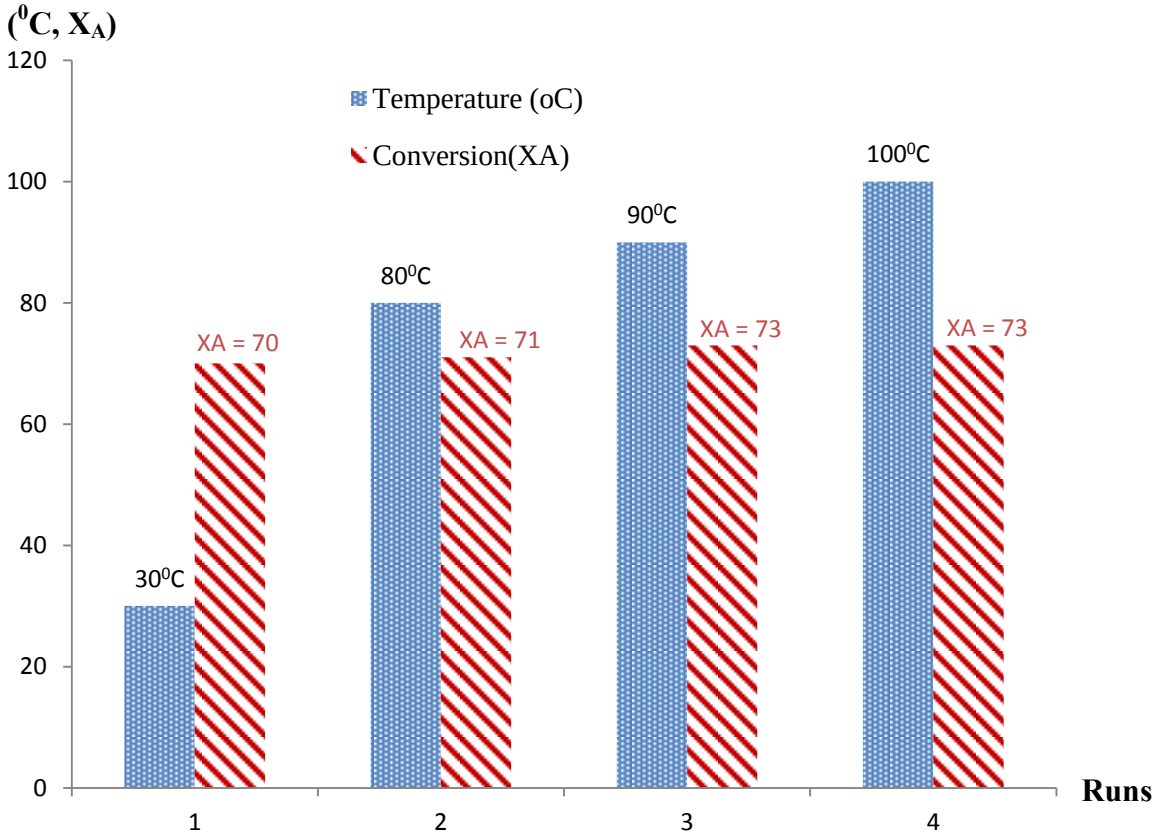


Figure 4.8: Effects of temperature on silica dissolution

An attempt made to investigate whether or not, this silica required high temperature before it can be dissolve as was always the case for the crystalline silica use in the production of the

commercial zeolite grade silica sol shows that temperature was not a critical parameter for the dissolution. Figure 4.8showed 70% dissolution at 30^0C and 73% at 100^0C.

4.4.3 Reactor design/specifications

The batch information of the designed and fabricated pilot plant is presented in Table 4.9 which requires 5.0kg silica, 2.5kg sodium hydroxide to produce 6.6kg sodium silicate with 88.4% yield. Table 4.10 presents the summary of the design calculations of the pilot plant unit with production capacity of about 10 liters per batch. The detail design calculations are presented as Appendix A.

Table 4.9: Sodium Silicate Production Batch Information

MATERIAL	AVERAGE PER BATCH
Si/Na wt. ratio desired	2.4
Silica input	5000g
Caustic (Sodium hydroxide) input	2500g (50% wt)
Sodium Silicate output	6631g
Yield	88.4 wt.%

Table 4.10: Summary of Design Data

Material (frame, external containers)	Schedule 80, ANSI 304 SS
Material (internal reactor tanks)	Polypropylene
Superficial velocity	$0.01ms^{-1}$
Reactor diameter	0.2697m
Sand bed height	0.2779m
Reactor height	0.3500m
Production capacity	$0.00968m^3$
Total volume	$0.0200m^3$

A standard size (2mm thickness, 1inch diameter) plastic pipe was chosen, this was done to minimize the corrosion of the pipe due to alkaline attack and ensure purity of the final sodium silicate product. The pipe was properly lagged; hence the heat lost was very negligible. A plastic impeller pump with the power rating of 0.75 kW (adjustable) was selected based on the assumed

lost work due to friction in the piping and valves as well as the need to overcome the pressure drop as the viscosity of the slurry increased. Two stainless steel heating band with power rate and dimension: 660W and 4cm diameter was chosen and lined on a Teflon pipe to maintain the temperature of the reactor inlet. A vibrator was also selected and coupled to the base of the reactor to ease the flow of the viscose sodium silicate across the grid of the bed. A flow meter was proposed to monitor flow rate of sodium hydroxide/sodium silicate into the reactor.

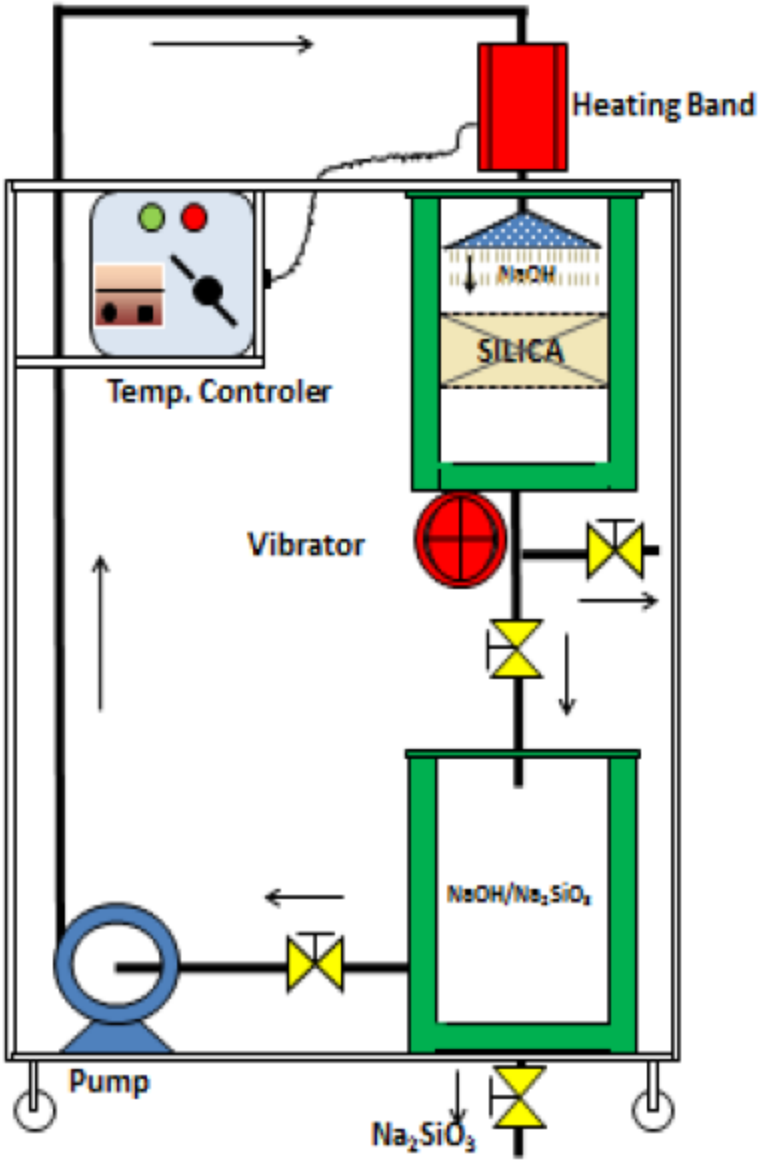


Figure 4.9: Schematic flow diagram of the sodium silicate production pilot plant

A schematic flow diagram of the sodium silicate production pilot plant was produced as shown in Figure 4.9 which gave the whole idea of how the various components aforementioned had to be arranged after the fabrication. This combined with the calculated values were utilized and a detail drawing of the pilot plant was produced as presented in Figure 4.10. The drawing was used as a guide during the fabrication period. Before fabrication started at HANIGHA Nigeria Kakuri Kaduna under the close supervisor of the research team, all the materials required and the units specified were purchased from within and outside the country.

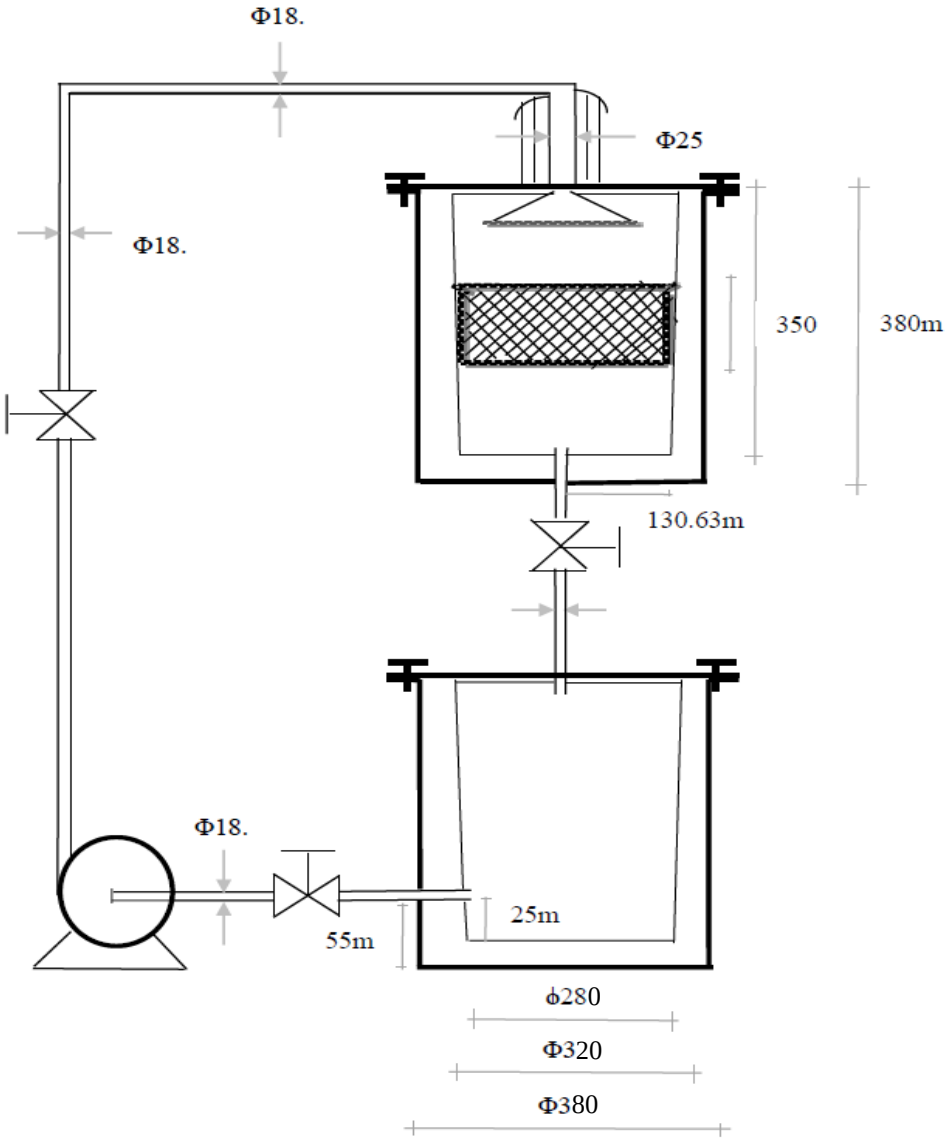


Figure 4.10: Front view drawing of the sodium silicate production pilot plant



Plate 4.2: Pilot plant for the production of sodium silicate from kaolin

The fabricated sodium silicate pilot plant is shown in Plate 4.2. In addition to the objective of this work, higher volume (≤15 liters) and lower grade sodium silicate can be produced per batch using the unit, that was the idea behind the wide margin of 50% (i.e. 20 liters total volume of the holding tank) given to take that into cognizance.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the investigation carried out the following conclusions were drown:

I. A stable zeolite grade silica sol with less trace contaminants as compared to the commercial silica sol though with less concentration has been prepared from Kankara kaolin.

II. 2.5/2.5 fold double dealumination was chosen as the best treatment option for meta-kaolin to prepare pure silica as the raw material for sodium silicate production.

III. First order reaction described the kinetics of silica dissolution in sodium hydroxide with reaction rate constant of 1.7798/min.

IV. Na-ZSM-5 was successfully synthesized from Kankara kaolin based silica sol; the XRD pattern conformed well to XRD pattern of the standard and commercial Na-ZSM-5.

V. The silica to alumina ratio of the synthesized zeolites fell within the range for ZSM-5 (eight to infinity).

VI. Sodium silicate production pilot plant was developed with the capacity of 10 liters of sodium silicate in a single batch of 3hrs.

5.2 Recommendations

I. From the work carried out, I wish to make the following recommendations.

II. Further analyses like Zeta Potential, TEM and Accelerated Aging Test should be carried out to fully characterize the silica sol.

III. Further research work is required to test the possibilities of producing silica sol from Kankara kaolin with better or similar qualities using other methods such as ion exchange.

IV. Federal government should expedite action on establishing sodium silicate production plant due to its vast applications and high demand. In addition, a silica sol production plant should be set up as a complement. This, apart from provision of job opportunities to our teeming unemployed youths and solving the problem faced by zeolite researchers, will also serve as a means of income generation and boost the economy of the country.

REFERENCES

Ahlberg, J.E. and Simpson, E.A. (1959). Preparation of Silica Sols, (W.R. Grace & Co.) US Pat.2.900.348.

Ajayi, O. A. and Adefila, S. S. (2012).Comparative Study of Chemical And Biological Methods of Beneficiation of Kankara Kaolin.*International Journal of Scientific & Technology Research*.Volume 1, Issue 8

Alexander, G.B. (1956). Process for Producing sols of 5-8 Milimicrons Silica Particles and Product, (Du Pont), US Pat. 2.750.345.

Ana, M. S., Leila, V., Claudia, M. and Cristina, F. (2009).Silica Sol Obtained From Rice Husk Ash. *Chemistry & Chemical Technology*. Volume 3, No. 4

Atta, A.Y., Ajayi, O.A. and Adefila, S. (2007). Synthesis of Faujasite Zeolites from Kankara Kaolin Clay.*Journal of Applied Sciences Research*, 3(10): 1017-1021

Bechtold, M. F. and Synder, O. E. (1951). Chemical Processes and Composition, (Du Pont), US Pat.2.574.902.

Bird, P.G. (1941). Colloidal Solutions of Inorganic Oxides, (National Aluminate Co). US Pat. 2.244.325

Brinker, C. J. and Scherer, G. W. (1990). The Physics and Chemistry of Sol-Gel-Science, *Academic press*, San Diego

Brykov, A.S. (2004). Formation of concentrated Polysilicate Solutions from Stabilized Silica Sols, *Colloid Journal*, 66, 481-486.

Carman, P. C. (1940). Constitution of Colloidal Silica. Trans Faraday Soc., 36, 964-973

Cheri, W. C., Rodman D. L., Joseph F. S., Leonardo R. A., Hee-Jung I., Yihui Y., Jason C. C. andZi-Ling, X. (2005).A Method for the Preparation of Transparent Mesoporous Silica Sol–Gel Monoliths Containing Grafted Organic Functional Groups. *Journal of Materials Chemistry*,www.rsc.org/materials

Chou, K. S. and Chen, C. C. (2006). Preparation of Monodispersed Silica Colloids Using Sol-Gel Method: Cosolvent Effect. Book title "Innovative Processing and Synthesis of Ceramics, Glasses and Composites VIII, Volume 166". 10/18/

Colina, F. G., Llorens, J. (2007). Study of the Dissolution of Dealuminated Kaolin in Sodium Potassium Hydroxide During the Gel Formation Step in Zeolite X Synthesis. Microporous Mesoporous Mater 100:302–311

Comb, L.F. (1996). Silica – Silica Chemistry and Reverse Osmosis, *Ultrapure Water*, 41.

Dimitar, G., Bogdan, B., Krasimira, A., Irena, M. and Yancho, H. (2009). Synthetic zeolites - Structure, Clasification, Current Trends in Zeolite Synthesis Review. International Science Conference, Stara Zagora, Bulgaria

Feng, H., Li, C., Shan, H. (2009). In-situ Synthesis and Catalytic Activity of ZSM-5 Zeolite. Appl Clay Sci 42:439–445

Gaishun, V.E., Tulenkova, O.I., Melnichenko, I.M., S.A. Baryshnin, Potapenok, Y.A., Xlebokazov, A. P. andStręk, W. (2000). Preparation and Properties of Colloidal Nanosize Silicadioxide for Polishing of Monocrystalline Silicon Wafers. *Materials Science*, Volume 20, No. 2

Hetherington, G. and Jack, K. H. (1962).Water in Vitreous Silica. Part I. Influence of "Water" Content on the properties of Vitreous Silica. Phys. Chem. Glasses 3, 129-133.

http://www.blueleaftsoftware.com/products/Dagra/Trial.php

Hyung, M. L.,Jinho, L., Jeong-Hwan, J., Seong-Geun, O. andSeung-Ho, L.(2010).Comparative Study of Various Preparation Methods of Colloidal Silica. *Scientific Research*, *Engineering*, 2, 998-1005, www.scirp.org/journal/eng

Iler,R. K. (1979). The Chemistry of Silica-Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. Wiley, New York, 331-337.

Karami, A., Vahdany G. R., Abedi M. andFattahi, M. (2008).Preparation and Characterization of Colloidal Silica in Alkaline and Constant Range of pH.*Iran. J. Chem. Chem. Eng.*,Volume 27, No. 4

Khatamian, M., Irani, M. (2009) Preparation and Characterization of Nanosized ZSM-5 Zeolite using Kaolin and Investigation of Kaolin Content, Crystallization Time and Temperature Changes on the Size and Crystallinity of Products. *J Iran Chem Soc* 6:187–194

Kitahara, S. (1960). The Polymerization of Silicic Acid Obtained by Hydrothermal Treatment of Quartz and Solubility of Amorphous Silica. Rev. Phys. Chem. Japan. 30, 131-137

Kitchener, J. A., Mackenzie, J. D. and Bockris, J. O. M. (1955).Viscous Flow in Silica and Binary Liquid Silicates. Trans. Farad. Soc. 51, 1734-1748.

Kovo, A. S., Hernandez, O., Holmes, S. M. (2009) Synthesis and Characterization of Zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a Novel, Lower Temperature, Metakaolinization Technique. J Mater Chem 19:6207–6212

Kruyt, H. R. and Postma, J. (1979). The Silicic Acid Sol. Wiley, New York.

Lee,Y. K., Yoon,Y. R. andRhee, H. K. (2000). Preparation of Colloidal Silica Using Peptization Method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume173, No. 1,109-116.

Legally, G. (2000). Silicate. Ullmann's Encyclopedia of Industrial Chemistry, 15th Edition

Lisensky, G. and Blitz, I. (2010). Preparation of Zeolite ZSM5 and Catalysis of Xylene Isomerization, 2008 the Board of Regents of the University of Wisconsin System. http://www.chemistry.binghamton.edu/chem445/zsm5/zsm5.htm.\

Moulson, A. J. and Robert, J. P. (1960). Water in Silica Glass Ceramic Division, Houldsworth School of Applied Science, The University, Leeds.

Nittaya, T. andApinon, N. (2008). Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method. *Chiang Mai J. Sci.* 35(1): 206-211, www.science.cmu.ac.th/journal-science/josci.html

Okamoto, G. Okura, T. and Goto, K. (1957). Properties of Silica in Water. Geochim. Cosmochin. Acta, 12, 123-132

Peter, G. (2012). Use and Production of Silica Nanoparticles; Nano Connect Meeting. Helsingborg.

Rana, Th. Abd A., (2013). Generation and Characterisation of Catalytic Films of Zeolite Y and ZSM-5 on FeCrAlloy Metal. University of Manchester, UK.

Research and Development, (2010). Research on Development and Applications of silica sol. China Silicon Industry, Volume 3 No. 6

Robert, D. J. and Curran, M. S. (1989). Preparation of silica sols. Nalco Chemical Company, Naperville, III. US Pat.4,806, 665

Robinson, J. W. (1946). Silicic Acid and Processes for Producing Same. (Du Pont), US Pat 2.392.767.

Sanhueza, V., Kelm, U., Cid, R. (1999) Synthesis of Molecular Sieves from Chilean Kaolinites: 1. Synthesis of NaA Type Zeolites. *J Chem Technol Biotechnol* 74:358–363

Savitri, O., Yuni K. K., Iman, A. and Riwandi, S. (2012). The Effect of Alkaline Treatment to the Structure of ZSM5 Zeolites.*Makara Journal of Science* 16/3, 155-162

Sosman, R.B. (1965). The Phases of Silica. New Brunswick. Rutger University Press. New Jersey, 138-156

Sushama, M. K. (2002). Halogenation and Isomerization Reactions of Aromatics Over K-L, H-Beta and H-ZSM-5 Zeolite Catalysts.Catalysis Division National Chemical Laboratory Pune 411 008, India

Ulrich, G. (2004). Chemical Engineering Design and Economics: A practical Guide. Boca Raton: CRC Press

Vysotskii, Z.Z. and Strazhesko, D.N. (1973). Isoelectric State of Disperse Silicas and Ion Exchange in Acid Solutions. Adsorpt. Adsorbents, 1, 55–71

Weres, O., Yee, A. and Tsao, L. (1981). Kinetics of Silica Polymerization. *Journal of Colloid and Interscience*, 84:379-402

Weyl, W. A. and Marboe, E. C. (1964). The Constitution of Glasses, a Dynamic Interpretation, volume 1, Interscience, New York

Willey, J. D. (1974). The Effect of Pressure on the Solubility of Amorphous Silica in Seawater at ^{0}C. Mar. Chem. 2, 239-250

Wilson, A., Gustavo, G., Jonas, H. and Johanne, M. (2014). Comparison Between Leached Metakaolin and Leached Diatomaceous Earth as Raw Materials for the Synthesis of ZSM-5. SpringerPlus, 3:292. http://www.springerplus.com/content/3/1/292 \

APPENDICIS

APPENDIX A

A1: Holding Tank Sizing

Volume of Raw Materials:

$$VNaOH = \frac{m_{NaOH}}{\rho_{NaOH}} VNaOH = \frac{2.5kg}{1560kg/m3} = 1.6026\text{x}10^{-3}\text{m}^3$$

$$VH2O = \frac{m_{H2O}}{\rho_{H2O}} \qquad VH2O = \frac{5.0kg}{1000kg/m3} = 5.0\text{x}10^{-3}\text{m}^3$$

$$VSiO2 = \frac{mSiO2}{\rho SiO2} \qquad VSiO2 = \frac{4.69375kg}{1530kg/m3}\ 3.0678\text{x}10^{-3}\text{m}^3$$

Tank Volume

$$V_{Tank} = V_{NaOH} + V_{H2O} + V_{SiO2}$$

$$V_{Tank} = (1.6026 + 5.0 + 3.0678)\text{x}10^{-3}\text{m}^3$$

$V_{Tank} = 9.6704 \text{ x } 10^{-3}\text{m}^3$

A2: Mass Balance

Stoichiometric Equation:

$$NaOH + xSiO_2 + H_2O \longrightarrow Na_2O\,(SiO_2)_x + H_2O$$

The *x's* in the equation represent the different grades of sodium silicate which can be produced from this reaction. For most zeolites synthesis the average grade used is 2.44. To convert this to mole percent the following equation is used.

$R_m = 1.032R_w$ (Legally G., 2000)

$$R_m = 1.032 \times 2.44 \approx 2.5$$

Therefore, stoichiometric equation

$$2NaOH + 2.5SiO_2 + H_2O \longrightarrow Na_2O\,(SiO_2)_{2.5} + 2H\,O$$

Mole Calculation:

What was imputed,

$$n_{NaOH} = \frac{m_{NaOH}}{M_{NaOH}} = \frac{2.5kg}{40kg/kgmol} = 6.25 \times 10^{-2}\text{kgmol}$$

$$n_{SiO2} = \frac{m_{SiO2}}{M_{SiO2}} = \frac{5.0kg}{60.08kg/kgmol} = 8.32 \times 10^{-2}\text{kgmol}$$

What is required (from thestoichiometric equation)

$$n_{NaOH} = n_{SiO2}\left(\frac{mole\ fraction\ NaOH}{mole\ fraction\ SiO2}\right) = 8.32 \times 10^{-2}\text{kgmol}\left(\frac{2.0}{2.5}\right) = 6.657 \times 10^{-2}\text{kgmolNaOH}$$

$$n_{SiO2} = n_{NaOH}\left(\frac{mole\ fraction\ SiO2}{mole\ fraction NaOH}\right) = 6.25 \times 10^{-2}\text{kgmol}\left(\frac{2.5}{2.0}\right) = 7.812 \times 10^{-2}\text{kgmol } SiO_2$$

Since 6.657×10^{-2}kgmol NaOH is required but there is only 6.25×10^{-2}kgmol, then NaOH is the limiting reactant. Whereas 7.812×10^{-2}kgmol of $SiO_2$is needed but there is 8.32×10^{-2}kgmol present, therefore SiO_2 is the excess reactant.

Excess Silica:

$$n_{SiO2} = (8.32 - 7.8125) \times 10^{-2}\text{kgmol}$$

$$n_{SiO2} = 5.075 \times 10^{-3}\text{kgmol}$$

Mole of sodium silicate produced

$$n_{Na2O(SiO2)2.5} = n_{NaOH}\left(\frac{mole\ fraction\ Na2O(SiO2)2.5}{mole\ fraction NaOH}\right) = 6.25 \times 10^{-2}\text{kgmol}\left(\frac{1}{2}\right) = 3.125\text{x } 10^{-2}\text{kgmol}Na_2O(SiO_2)_{2.5}$$

Hence, mass of sodium silicate produced;

$$n_{Na2O(SiO2)2.5} = \frac{mNa2O(SiO2)2.5}{MNa2O(SiO2)2.5}$$

$$m_{Na2O(SiO2)2.5} = M_{Na2O(SiO2)2.5} x n_{Na2O(SiO2)2.5}$$

$$m_{Na2O(SiO2)2.5} = 212.2\text{kg/kgmol} \times 3.12510^{-2}\text{kgmol}$$

$$m_{Na2O(SiO2)2.5} = 6.63125\text{kg } Na_2O(SiO_2)_{2.5}$$

APPENDIX B

B1: Data for X-Ray Diffraction Analysis of the Na-ZSM-5 Sample from Commercial Silica Sol

Some of the measurement conditions:

Anode material	Cu
K-Alpha1-wavelengh	1.54058
K-Alpha 2-wavelengh	1.544426
Ratio K-Alpha2/K-Alpha1	0.5
Divergence slit	Fixed, 0.38mm
Monochromator used	No
Generator voltage	40
Tube current	30
Scan axis	Gonio
Scan range	5.00100 to 70.01218
Scan step size	0.0835563
No. of points	778
Scan type	Continuous
Time per step	15.24

Table B1: XRD data for Na-ZSM-5 from commercial zeolite grade silica sol

Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)
5.124	433.6	5.628	456.9	6.132	360.4
5.208	479	5.712	419.4	6.216	369.8
5.292	449.5	5.796	359.6	6.3	343.1
5.376	420.3	5.88	398.4	6.384	383.5
5.46	393.2	5.964	368.2	6.468	339.8
5.544	404	6.048	373.6	6.552	385.7

6.636	378.4	9.996	283	13.356	276.2
6.72	342.9	10.08	280.9	13.44	214.1
6.804	356.2	10.164	241.5	13.524	186.4
6.888	382.3	10.248	239.5	13.608	218.2
6.972	385	10.332	230.6	13.692	279.5
7.056	379.6	10.416	221.9	13.776	322.9
7.14	425.1	10.5	253.9	13.86	414.2
7.224	442.9	10.584	219.9	13.944	498.2
7.308	517.4	10.668	205.8	14.028	443.7
7.392	590.6	10.752	203.6	14.112	316.8
7.476	711.9	10.836	202.7	14.196	254.3
7.56	867.1	10.92	198.2	14.28	237.6
7.644	1150	11.004	227.9	14.364	230
7.728	1623	11.088	218.1	14.448	237.3
7.812	2240.6	11.172	213.7	14.532	282.7
7.896	3162.7	11.256	213.8	14.616	368.5
7.98	3460.9	11.34	205.1	14.7	477
8.064	2016.4	11.424	206.2	14.784	635
8.148	979.5	11.508	187	14.868	703.6
8.232	673.9	11.592	211.3	14.952	578.3
8.316	621.8	11.676	212	15.036	381.5
8.4	653.5	11.76	246.4	15.12	273.8
8.484	753.3	11.844	259.5	15.204	257.7
8.568	883.2	11.928	231.6	15.288	254.5
8.652	1212.6	12.012	215.6	15.372	275.2
8.736	1582	12.096	200.8	15.456	355.6
8.82	2021.5	12.18	205.3	15.54	424
8.904	1968.9	12.264	209.8	15.624	427.6
8.988	1492.1	12.348	219.4	15.708	354.6
9.072	1071.9	12.432	230	15.792	397.5
9.156	792.7	12.516	208.7	15.876	483.4
9.24	553.8	12.6	197.6	15.96	527
9.324	436.4	12.684	198.8	16.044	430
9.408	365.7	12.768	189.6	16.128	314.2
9.492	323.2	12.852	201.8	16.212	248.3
9.576	326.2	12.936	228.3	16.296	203.2
9.66	304.9	13.02	234.8	16.38	209.8
9.744	280.5	13.104	263.2	16.464	234.8
9.828	291.1	13.188	318.6	16.548	255.9
9.912	283.8	13.272	340	16.632	250.1

16.716	212.6	20.076	174	23.436	1183
16.8	176.3	20.16	194.2	23.52	751
16.884	173.4	20.244	218.3	23.604	708.6
16.968	174.6	20.328	250.8	23.688	825.7
17.052	166.7	20.412	304.6	23.772	956.2
17.136	169.1	20.496	287.2	23.856	998.5
17.22	201.2	20.58	229.1	23.94	1142.5
17.304	221.6	20.664	252.7	24.024	1134.8
17.388	195.9	20.748	279	24.108	758.2
17.472	224.4	20.832	338.9	24.192	558.5
17.556	233.2	20.916	347.8	24.276	550
17.64	293.8	21	276.8	24.36	607.2
17.724	359.1	21.084	214.2	24.444	678.3
17.808	366.8	21.168	174.5	24.528	576.3
17.892	315.9	21.252	146.2	24.612	487.3
17.976	243.9	21.336	124.1	24.696	359.8
18.06	211.4	21.42	135	24.78	257.4
18.144	183.9	21.504	136.1	24.864	253.7
18.228	154	21.588	153.3	24.948	231.8
18.312	154.4	21.672	178.9	25.032	206
18.396	143.8	21.756	176.5	25.116	163.1
18.48	156.5	21.84	198	25.2	180.7
18.564	139.5	21.924	163.9	25.284	162.3
18.648	130	22.008	191.1	25.368	165.3
18.732	152.3	22.092	242	25.452	192.3
18.816	148.6	22.176	242	25.536	210.3
18.9	160.5	22.26	241.4	25.62	252.4
18.984	171.5	22.344	230.5	25.704	287.3
19.068	168.7	22.428	222.4	25.788	300.7
19.152	203.2	22.512	214.4	25.872	307
19.236	260	22.596	224.1	25.956	332.3
19.32	254.1	22.68	280.1	26.04	294.5
19.404	202.1	22.764	370.9	26.124	269.4
19.488	162.4	22.848	510.4	26.208	252.2
19.572	148.3	22.932	818.9	26.292	257.2
19.656	148.8	23.016	1432.5	26.376	246.7
19.74	165.1	23.1	2062.2	26.46	272.1
19.824	175.1	23.184	2231.6	26.544	312.2
19.908	187.8	23.268	1891.4	26.628	331.7
19.992	185.4	23.352	1548.1	26.712	336.3

26.796	336.7	30.156	388.4	33.516	127.8
26.88	353.5	30.24	344.8	33.6	112
26.964	367.7	30.324	320.4	33.684	106.2
27.048	321.2	30.408	294.4	33.768	127.9
27.132	261.6	30.492	261.5	33.852	118.2
27.216	238.7	30.576	225.7	33.936	103.7
27.3	227.3	30.66	180	34.02	118.6
27.384	220	30.744	145.9	34.104	131.8
27.468	237.6	30.828	142.6	34.188	122.7
27.552	218.5	30.912	139.6	34.272	142
27.636	189	30.996	140.3	34.356	170
27.72	170.6	31.08	146.7	34.44	184.1
27.804	180.7	31.164	155.2	34.524	171.1
27.888	189.5	31.248	146.5	34.608	158
27.972	185.6	31.332	139	34.692	166.9
28.056	176.6	31.416	144.1	34.776	146.1
28.14	178.2	31.5	135.5	34.86	165.8
28.224	193.8	31.584	137.4	34.944	155.4
28.308	191.4	31.668	126.4	35.028	151.3
28.392	198.2	31.752	118	35.112	144.1
28.476	190.3	31.836	126.6	35.196	136
28.56	170.1	31.92	125.7	35.28	134.1
28.644	171.8	32.004	121.7	35.364	119.9
28.728	167.1	32.088	135.2	35.448	138.4
28.812	163.6	32.172	149.5	35.532	140.1
28.896	146.3	32.256	137.2	35.616	121.1
28.98	154.1	32.34	129.3	35.7	159.7
29.064	205.1	32.424	117.8	35.784	170.4
29.148	258.8	32.508	129.9	35.868	174.7
29.232	302.5	32.592	139.1	35.952	147.4
29.316	338.1	32.676	162.1	36.036	185.7
29.4	323.4	32.76	176	36.12	187.1
29.484	268.3	32.844	176.6	36.204	187
29.568	238.8	32.928	161.4	36.288	208.7
29.652	219	33.012	142	36.372	161.7
29.736	258.6	33.096	122.9	36.456	131.4
29.82	351.5	33.18	109.8	36.54	153
29.904	411.2	33.264	110.8	36.624	121.2
29.988	438.5	33.348	114.3	36.708	127.7
30.072	446.3	33.432	121.9	36.792	121.2

36.876	120	40.236	106.7	44.184	80.4
36.96	157.4	40.32	93.8	44.268	83.3
37.044	134.2	40.404	97.8	44.352	77.7
37.128	156.9	40.488	102.7	44.436	83.2
37.212	215	40.572	105.4	44.772	103.9
37.296	180.9	40.656	98.3	44.856	139.8
37.38	171	40.74	113.4	44.94	181.6
37.464	173.4	40.824	92.7	45.024	229.2
37.548	196.2	40.908	110.8	45.108	254.5
37.632	201.6	40.992	110.8	45.192	265.1
37.716	151	41.076	120.8	45.276	257.1
37.8	149	41.16	114.2	45.36	252.5
37.884	99.4	41.244	110.7	45.696	214.9
37.968	109	41.328	97.2	45.78	169
38.052	109	41.412	99	45.948	124.2
38.136	109.3	41.496	112.2	46.032	135.7
38.22	114	41.58	112.2	46.116	121.2
38.304	113.1	41.664	100.7	46.2	115.3
38.388	101.5	41.748	108.3	46.284	109.1
38.472	105.4	41.832	102	46.368	120.7
38.556	77.8	41.916	96.4	46.452	135
38.64	99.2	42	91.1	46.536	131.5
38.724	120.7	42.084	91.6	46.704	107.8
38.808	116	42.168	108.3	46.788	91.1
38.892	99.1	42.252	99.3	46.872	98.2
38.976	107.2	42.336	105.2	46.956	96.8
39.06	98.7	42.672	91	47.04	91
39.144	85.9	42.756	97.7	47.124	107.3
39.228	118.7	42.84	113.6	47.544	132
39.312	102.1	42.924	109.5	47.964	89.8
39.396	94.6	43.008	100.5	48.048	84.7
39.48	86	43.092	121.1	48.132	69.8
39.564	87.6	43.176	127.2	48.552	131.7
39.648	95.3	43.428	102.2	48.72	133.3
39.732	87.6	43.512	114	48.972	115.7
39.816	92.7	43.596	122.5	49.056	100.5
39.9	77.9	43.848	101.8	49.56	96.4
39.984	88.4	43.932	106.8	49.644	118.7
40.068	96.6	44.016	99.9	49.98	109.5
40.152	105.1	44.1	80.5	50.064	95.7

B2: Data for X-Ray Diffraction Analysis of Na-ZSM-5 Sample from Kankara Kaolin

Some of the measurement conditions:

Anode material	Cu
K-Alpha1-wavelengh	1.54058
K-Alpha 2-wavelengh	1.544426
Ratio K-Alpha2/K-Alpha1	0.5
Divergence slit	Fixed, 0.38mm
Monochromator used	No
Generator voltage	40
Tube current	30
Scan axis	Gonio
Scan range	3.00000 to70.01218
Scan step size	0.0835563
No. of points	802
Scan type	Continuous
Time per step	8.89

Table B2: XRD data for Na-ZSM-5 from Kankara kaolin

Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)
3.04177817	475	3.793785146	317	4.545792122	286
3.125334501	389	3.877341477	283	4.629348453	251
3.208890831	448	3.960897807	292	4.712904783	242
3.292447162	427	4.044454138	317	4.796461114	251
3.376003493	360	4.128010469	302	4.880017445	257
3.459559823	378	4.211566799	302	4.963573775	305
3.543116154	317	4.29512313	249	5.047130106	220
3.626672485	330	4.378679461	322	5.130686437	228
3.710228815	307	4.462235791	262	5.214242767	251

5.297799098	246	8.640052324	625	11.98230555	185
5.381355429	237	8.723608655	949	12.06586188	115
5.464911759	262	8.807164986	1682	12.14941821	125
5.54846809	208	8.890721316	1496	12.23297454	123
5.632024421	224	8.974277647	542	12.31653087	119
5.715580751	224	9.057833978	659	12.4000872	123
5.799137082	224	9.141390308	637	12.48364354	177
5.882693412	234	9.224946639	208	12.56719987	147
5.966249743	258	9.30850297	182	12.6507562	121
6.049806074	213	9.3920593	167	12.73431253	122
6.133362404	220	9.475615631	209	12.81786886	119
6.216918735	230	9.559171962	207	12.90142519	128
6.300475066	222	9.642728292	181	12.98498152	136
6.384031396	230	9.726284623	183	13.06853785	153
6.467587727	223	9.809840954	202	13.15209418	219
6.551144058	212	9.893397284	186	13.23565051	291
6.634700388	212	9.976953615	160	13.31920684	144
6.718256719	193	10.06050995	152	13.40276317	129
6.80181305	219	10.14406628	149	13.4863195	129
6.88536938	220	10.22762261	155	13.56987583	126
6.968925711	222	10.31117894	128	13.65343216	122
7.052482042	234	10.39473527	162	13.7369885	174
7.136038372	217	10.4782916	147	13.82054483	249
7.219594703	247	10.56184793	125	13.90410116	414
7.303151034	284	10.64540426	137	13.98765749	341
7.386707364	326	10.72896059	140	14.07121382	110
7.470263695	382	10.81251692	133	14.15477015	138
7.553820026	410	10.89607325	149	14.23832648	123
7.637376356	599	10.97962958	129	14.32188281	140
7.720932687	764	11.06318591	137	14.40543914	121
7.804489018	1183	11.14674224	147	14.48899547	153
7.888045348	2158	11.23029858	140	14.5725518	193
7.971601679	3090	11.31385491	132	14.65610813	261
8.05515801	426	11.39741124	118	14.73966446	358
8.13871434	305	11.48096757	137	14.82322079	457
8.222270671	257	11.5645239	147	14.90677712	260
8.305827002	284	11.64808023	133	14.99033346	167
8.389383332	295	11.73163656	147	15.07388979	106
8.472939663	347	11.81519289	179	15.15744612	138
8.556495994	461	11.89874922	275	15.24100245	126

15.32455878	144	18.666812	69	22.00906523	93
15.40811511	171	18.75036833	84	22.09262156	141
15.49167144	238	18.83392467	80	22.17617789	200
15.57522777	296	18.917481	65	22.25973422	217
15.6587841	185	19.00103733	88	22.34329055	132
15.74234043	138	19.08459366	129	22.42684688	92
15.82589676	208	19.16814999	126	22.51040321	133
15.90945309	373	19.25170632	238	22.59395955	125
15.99300942	328	19.33526265	208	22.67751588	123
16.07656575	134	19.41881898	132	22.76107221	155
16.16012208	100	19.50237531	84	22.84462854	216
16.24367842	91	19.58593164	88	22.92818487	360
16.32723475	114	19.66948797	84	23.0117412	952
16.41079108	106	19.7530443	77	23.09529753	2164
16.49434741	147	19.83660063	92	23.17885386	1818
16.57790374	167	19.92015696	96	23.26241019	1608
16.66146007	99	20.00371329	132	23.34596652	1257
16.7450164	88	20.08726963	115	23.42952285	352
16.82857273	104	20.17082596	99	23.51307918	261
16.91212906	92	20.25438229	130	23.59663551	320
16.99568539	68	20.33793862	222	23.68019184	668
17.07924172	89	20.42149495	283	23.76374817	648
17.16279805	104	20.50505128	114	23.84730451	538
17.24635438	159	20.58860761	106	23.93086084	1012
17.32991071	148	20.67216394	133	24.01441717	1058
17.41346704	110	20.75572027	198	24.0979735	321
17.49702337	103	20.8392766	335	24.18152983	178
17.58057971	160	20.92283293	301	24.26508616	286
17.66413604	208	21.00638926	115	24.34864249	427
17.74769237	183	21.08994559	88	24.43219882	781
17.8312487	242	21.17350192	83	24.51575515	461
17.91480503	136	21.25705825	87	24.59931148	194
17.99836136	100	21.34061459	102	24.68286781	144
18.08191769	104	21.42417092	66	24.76642414	134
18.16547402	89	21.50772725	70	24.84998047	170
18.24903035	88	21.59128358	95	24.9335368	122
18.33258668	88	21.67483991	126	25.01709313	103
18.41614301	73	21.75839624	130	25.10064947	91
18.49969934	66	21.84195257	136	25.1842058	85
18.58325567	77	21.9255089	79	25.26776213	110

25.35131846	93	28.69357168	88	32.03582491	87
25.43487479	89	28.77712801	85	32.11938124	70
25.51843112	113	28.86068434	73	32.20293757	74
25.60198745	194	28.94424068	93	32.2864939	68
25.68554378	182	29.02779701	98	32.37005023	80
25.76910011	149	29.11135334	130	32.45360656	83
25.85265644	190	29.19490967	156	32.53716289	84
25.93621277	303	29.278466	277	32.62071922	70
26.0197691	220	29.36202233	266	32.70427556	93
26.10332543	132	29.44557866	129	32.78783189	126
26.18688176	102	29.52913499	95	32.87138822	137
26.27043809	133	29.61269132	85	32.95494455	79
26.35399443	138	29.69624765	77	33.03850088	69
26.43755076	144	29.77980398	113	33.12205721	72
26.52110709	141	29.86336031	213	33.20561354	64
26.60466342	202	29.94691664	329	33.28916987	49
26.68821975	231	30.03047297	337	33.3727262	69
26.77177608	230	30.1140293	264	33.45628253	107
26.85533241	205	30.19758564	192	33.53983886	89
26.93888874	205	30.28114197	136	33.62339519	65
27.02244507	294	30.3646983	182	33.70695152	68
27.1060014	153	30.44825463	152	33.79050785	79
27.18955773	76	30.53181096	95	33.87406418	83
27.27311406	81	30.61536729	89	33.95762052	80
27.35667039	121	30.69892362	79	34.04117685	65
27.44022672	140	30.78247995	68	34.12473318	66
27.52378305	159	30.86603628	64	34.20828951	72
27.60733939	118	30.94959261	59	34.29184584	96
27.69089572	99	31.03314894	83	34.37540217	149
27.77445205	91	31.11670527	87	34.4589585	147
27.85800838	87	31.2002616	83	34.54251483	113
27.94156471	84	31.28381793	106	34.62607116	92
28.02512104	104	31.36737426	70	34.70962749	125
28.10867737	99	31.4509306	74	34.79318382	96
28.1922337	110	31.53448693	85	34.87674015	98
28.27579003	100	31.61804326	59	34.96029648	85
28.35934636	122	31.70159959	53	35.04385281	108
28.44290269	102	31.78515592	59	35.12740914	88
28.52645902	133	31.86871225	59	35.21096548	103
28.61001535	128	31.95226858	76	35.29452181	77

35.37807814	69	38.72033136	81	42.06258459	35
35.46163447	44	38.80388769	79	42.14614092	40
35.5451908	73	38.88744402	64	42.22969725	47
35.62874713	89	38.97100036	72	42.31325358	55
35.71230346	114	39.05455669	49	42.39680991	55
35.79585979	123	39.13811302	43	42.48036624	53
35.87941612	111	39.22166935	59	42.56392257	65
35.96297245	80	39.30522568	43	42.6474789	68
36.04652878	103	39.38878201	47	42.73103523	54
36.13008511	149	39.47233834	43	42.81459157	64
36.21364144	166	39.55589467	54	42.8981479	80
36.29719777	93	39.639451	58	42.98170423	70
36.3807541	69	39.72300733	66	43.06526056	76
36.46431044	81	39.80656366	50	43.14881689	65
36.54786677	66	39.89011999	39	43.23237322	64
36.6314231	68	39.97367632	54	43.31592955	66
36.71497943	61	40.05723265	62	43.39948588	46
36.79853576	70	40.14078898	46	43.48304221	59
36.88209209	76	40.22434531	53	43.56659854	87
36.96564842	62	40.30790165	62	43.65015487	83
37.04920475	76	40.39145798	61	43.7337112	77
37.13276108	77	40.47501431	74	43.81726753	72
37.21631741	95	40.55857064	74	43.90082386	57
37.29987374	115	40.64212697	46	43.98438019	66
37.38343007	77	40.7256833	66	44.06793653	42
37.4669864	117	40.80923963	46	44.15149286	50
37.55054273	143	40.89279596	59	44.23504919	50
37.63409906	107	40.97635229	65	44.31860552	42
37.7176554	104	41.05990862	69	44.40216185	50
37.80121173	76	41.14346495	64	44.48571818	61
37.88476806	62	41.22702128	53	44.56927451	54
37.96832439	69	41.31057761	61	44.65283084	55
38.05188072	73	41.39413394	44	44.73638717	62
38.13543705	59	41.47769027	65	44.8199435	61
38.21899338	54	41.56124661	65	44.90349983	68
38.30254971	59	41.64480294	76	44.98705616	88
38.38610604	49	41.72835927	49	45.07061249	132
38.46966237	73	41.8119156	49	45.15416882	231
38.5532187	58	41.89547193	55	45.23772515	207
38.63677503	57	41.97902826	57	45.32128149	170

45.40483782	171	48.83064737	85		
45.48839415	231	48.9142037	80		
45.57195048	246	48.99776003	54		
45.65550681	166	49.08131637	49		
45.73906314	108	49.1648727	62		
45.82261947	72	49.24842903	43		
45.9061758	49	49.33198536	54		
45.98973213	62	49.41554169	53		
46.07328846	66	49.49909802	64		
46.15684479	65	49.58265435	50		
46.24040112	57	49.66621068	65		
46.32395745	66	49.74976701	53		
46.40751378	62	49.83332334	80		
46.49107011	77	49.91687967	76		
46.57462645	91	48.74709104	111		
46.65818278	99	48.83064737	85		
46.74173911	69	48.9142037	80		
46.82529544	79	48.99776003	54		
46.90885177	54	49.08131637	49		
46.9924081	43	49.1648727	62		
47.07596443	47	49.24842903	43		
47.15952076	44	49.33198536	54		
47.24307709	54	49.41554169	53		
47.32663342	68	49.49909802	64		
47.41018975	85				
47.49374608	102				
47.57730241	102				
47.66085874	88				
47.74441507	79				
47.82797141	62				
47.91152774	51				
48.16219673	44				
48.32930939	47				
48.41286572	62				
48.49642205	76				
48.57997838	80				
48.66353471	115				

C1: Simulated X-Ray Diffraction Data for Na-ZSM-5 Sample Generated using Dagra Blue Leaf Software (Version 2.0.12.35924)

Table C1: The simulated XRD data for Na-ZSM-5

Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)
5.380466	0.052855	9.849128	1.217927	14.9713	3.533593
7.023009	0.205057	9.905382	0.627869	14.99752	2.198883
7.442752	0.812493	9.970592	0.369503	15.02317	1.598263
7.633132	1.622322	10.16575	0.197285	15.50023	3.500341
7.67043	2.786397	10.36085	0.111205	15.87717	4.601569
7.745656	4.304759	10.55588	0.111246	15.90199	5.068727
7.810248	19.53886	10.88072	0.369707	15.95443	2.399302
7.853539	32.75333	10.9456	0.541977	16.91326	0.1305
7.999822	29.51777	10.94527	0.972619	17.89259	3.901299
7.998787	30.85248	11.07542	0.800396	17.97032	1.098412
7.998166	31.65331	11.85546	0.886695	17.94534	0.831459
8.013031	44.96712	11.98575	0.542212	18.82711	0.497981
8.076559	20.95605	12.05096	0.283841	18.9533	0.164331
8.165833	4.355472	12.24612	0.111628	19.15473	0.231111
8.282165	2.128587	12.37614	0.111659	19.96043	0.564975
8.587422	2.58416	12.70119	0.111732	20.08659	0.264687
8.625308	2.989056	12.83121	0.111763	20.43787	1.966534
8.662922	3.74824	12.96116	0.197917	21.01803	0.832159
8.66253	4.254359	13.09104	0.370208	21.0434	0.598588
8.728809	17.31216	13.16014	0.663539	22.15125	1.032619
8.765205	19.6403	13.336	1.230834	22.20066	2.267246
8.990269	12.42297	13.71454	0.263245	22.20051	2.467455
9.013786	14.41535	13.81507	0.530214	22.27681	1.499798
9.155067	9.518072	13.91307	4.067239	22.27718	1.032645
9.236924	2.483083	14.03976	3.099597	22.55458	0.56556
9.314114	1.470866	14.11733	0.49691	22.62996	0.799153
9.390945	0.91416	14.16786	0.296721	22.73083	0.632335
9.544066	0.5093	14.57055	0.663858	22.32778	0.732346
9.696913	0.458723	14.59555	0.897435	22.37839	0.432052
9.81124	0.813031	14.59537	1.131011	22.55458	0.56556
9.849128	1.217927	14.69612	1.131037	22.62996	0.799153
9.905382	0.627869	14.64546	1.49807	22.62996	0.799153
9.849128	1.217927	14.6956	1.798395	22.62996	0.799153
9.905382	0.627869	14.69544	1.998605	22.37839	0.432052
9.970592	0.369503	14.72024	2.49913	22.73083	0.632335
9.970592	0.369503	14.72024	2.49913	22.73083	0.632335

23.13473	31.92566	24.46807	1.404118	26.98605	2.205516
23.13512	31.42514	24.51857	1.237285	26.98638	1.771735
23.13538	31.09146	24.69485	1.270698	26.98649	1.638258
23.1361	30.15716	24.74511	1.40418	27.01087	2.672674
23.13636	29.82348	24.74529	1.170604	27.01054	3.106456
23.16212	29.08939	24.77028	1.437552	27.01025	3.473504
23.13747	28.38866	24.84617	1.003792	27.1119	2.305653
23.45742	5.541511	24.89677	0.703487	27.13734	1.971976
23.48305	4.974263	24.9474	0.369822	27.13763	1.604928
23.48354	4.340272	24.99788	0.236361	27.16356	0.637266
23.75846	7.076504	25.14902	0.203025	27.26443	0.470444
23.68288	7.109855	25.32532	0.203062	27.38022	0.937623
23.68321	6.676074	25.45107	0.43667	27.48057	1.438169
23.65875	5.741767	25.50129	0.63689	27.48083	1.104487
23.68446	5.07441	25.55138	1.003949	27.50623	0.837549
23.68492	4.473791	25.50067	1.437719	27.78366	0.337092
23.73566	4.006648	25.57623	1.437735	27.90972	0.17028
23.90989	6.676126	25.60175	1.003959	28.71562	0.237202
23.90945	7.243379	25.60203	0.636911	28.8416	0.170494
23.90907	7.743898	25.72796	0.636942	29.01788	0.203898
24.00218	17.58747	25.75292	0.937257	29.51999	2.272824
24.00272	16.88674	25.80297	1.337682	29.52033	1.839043
24.00272	16.88674	25.80267	1.738097	29.54585	1.405267
24.0034	16.01917	25.97783	3.206331	29.89739	2.773432
24.00446	14.65109	26.05339	3.206347	29.89711	3.14048
24.00554	13.24963	26.05359	2.939403	29.8968	3.54089
24.00596	12.71574	26.05385	2.605722	29.89651	3.907938
24.03393	9.112011	26.07922	2.372151	29.92126	4.475206
24.03453	8.344549	26.10459	2.138579	29.92087	4.975726
24.03499	7.743924	26.10479	1.871636	29.99434	7.678544
24.03574	6.776257	26.30696	1.004121	29.9947	7.211391
24.06157	5.942066	26.30711	0.803911	29.99496	6.877709
24.08728	5.274714	26.33245	0.603706	29.9953	6.443928
24.08769	4.740828	26.35774	0.47024	29.99566	5.976775
24.08806	4.273674	26.45856	0.370161	29.99625	5.209312
24.08842	3.806522	26.50875	0.603748	30.3006	2.473212
24.08875	3.372741	26.53376	0.83733	30.30027	2.906993
24.08917	2.838854	26.63404	1.437975	30.2999	3.374146
24.16516	2.271612	26.63424	1.171032	30.27449	3.67445
24.21515	2.772142	26.63448	0.870717	31.41018	0.671594
24.16516	2.271612	26.98605	2.205516	31.47449	3.67445
24.16516	2.271612	26.98638	1.771735	31.41018	0.671594

31.41034	0.471384	36.06962	0.639282	42.46136	0.073471
31.46087	0.27119	36.09459	0.906231	42.58708	0.340446
32.01503	0.17121	36.16997	1.139823	42.73833	0.173639
32.09052	0.271336	36.16966	1.540237	42.93982	0.173686
32.09044	0.371441	36.19451	1.974024	43.01522	0.373912
32.14075	0.438184	37.22773	1.206796	43.14125	0.240471
32.16574	0.705133	37.30329	1.206817	43.26708	0.373969
32.21621	0.571672	37.3036	0.806403	43.26692	0.574174
32.74457	1.272521	37.30381	0.539459	43.66992	0.540901
32.8205	0.805384	37.40458	0.506114	43.74556	0.440812
32.82023	1.139065	37.42963	0.672957	43.79611	0.207246
32.87087	0.805394	37.50501	0.906549	43.9473	0.107177
32.92101	1.10572	37.58072	0.70636	44.12355	0.173952
32.92139	0.6052	37.65612	0.906586	44.27462	0.240727
32.99695	0.605216	37.65589	1.206895	44.42579	0.17402
33.07272	0.338288	38.65818	0.206081	44.60214	0.107324
33.12327	0.104722	38.73355	0.439678	44.82871	0.240853
33.19875	0.204848	38.83447	0.206123	45.07985	1.175211
33.29959	0.071398	38.93522	0.206144	45.63319	2.143003
34.02984	0.271775	39.01065	0.373008	45.6328	2.643523
34.02971	0.438613	39.03578	0.439746	45.93674	0.441308
34.15582	0.205062	39.08641	0.106075	46.03738	0.5748
34.15574	0.305167	39.1871	0.172835	46.16352	0.307889
34.2314	0.171712	39.84197	0.139619	46.31464	0.30792
34.25646	0.338555	40.01832	0.072918	46.4152	0.541523
34.25628	0.572131	40.245	0.07297	46.46536	0.808476
34.30657	0.672252	40.42122	0.173117	46.99478	0.141239
34.33126	1.306248	40.52183	0.339976	47.14587	0.174637
34.35679	0.872467	40.57238	0.10641	47.67431	0.775381
34.40744	0.505435	41.00042	0.273352	47.72499	0.374977
35.61652	0.305496	41.12619	0.473583	47.90114	0.575224
35.64161	0.438978	41.1763	0.807275	48.0022	0.17483
35.69185	0.605827	41.25217	0.406881	48.50576	0.375155
35.71685	0.839409	41.37823	0.240069	48.95908	0.408626
35.7166	1.17309	41.45361	0.473656	49.0848	0.675595
35.71639	1.440033	41.45343	0.707233	49.0846	0.942538
35.79213	1.206472	41.57959	0.406954	49.13533	0.475395
35.76712	0.972891	41.7056	0.306875	49.61397	0.342034
35.79262	0.572481	41.882	0.173446	49.79029	0.308709
35.89365	0.205454	42.10873	0.10676	49.94152	0.175269
36.04467	0.338962	42.31019	0.140178	50.0674	0.242038

C2: X-Ray Diffraction Data for Na-ZSM-5 from Standard Method Generated using Dagra Blue Leaf Software (Version 2.0.12.35924)

Table C2: The XRD data of Na-ZSM-5 sample from standard method

Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)
5.068498	1.11495	8.176777	1.760348	10.11212	0.532827
5.127145	0.912473	8.176777	1.659109	10.11212	0.621411
5.537673	1.178225	8.11813	1.481941	10.17077	0.520172
5.537673	0.912473	8.176777	1.393357	10.28806	0.608756
5.77226	1.076986	8.176777	1.304773	10.28806	0.532827
5.77226	0.861853	8.176777	1.16557	10.40535	0.608756
6.006846	0.988402	8.235423	1.051676	10.58129	0.545482
6.065494	0.899818	8.235423	0.899818	10.58129	0.621411
6.769254	0.963092	8.294069	0.849198	10.75723	0.507517
6.710608	0.760614	8.352716	0.912473	10.81588	0.608756
6.827901	0.874508	8.411363	0.74796	10.93317	0.532827
7.003841	0.72265	8.470011	0.849198	11.05047	0.646721
7.179781	0.861853	8.587303	0.798579	11.10911	0.520172
7.297075	0.735305	8.64595	0.925127	11.22641	0.608756
7.414368	0.937782	8.64595	1.039021	11.3437	0.494862
7.531662	0.823888	8.64595	1.190879	11.40235	0.570791
7.590309	1.051676	8.704597	1.874242	11.51964	0.494862
7.648955	0.988402	8.763245	2.013445	11.57829	0.583446
7.648955	1.16557	8.821891	2.203268	11.69558	0.520172
7.648955	1.292118	8.880537	3.266276	11.75423	0.596101
7.707602	1.418667	8.939184	3.101763	11.87152	0.735305
7.707602	1.532561	8.99783	2.975214	11.93017	0.836543
7.824896	2.532294	8.939184	2.798046	12.04746	0.608756
7.824896	2.658843	8.99783	2.658843	12.04746	0.811234
7.824896	3.089108	9.056478	2.557604	12.10611	0.520172
7.883543	3.253621	9.173771	2.177958	12.28205	0.520172
7.883543	3.35486	9.232418	1.735038	12.3407	0.596101
7.883543	3.519373	9.173771	1.279464	12.51664	0.621411
7.824896	3.671232	9.232418	1.368047	12.57528	0.67203
7.883543	3.924329	9.349711	0.874508	12.92716	0.494862
7.942189	4.050877	9.408359	0.684685	12.98581	0.558137
7.942189	5.999725	9.467005	0.811234	13.1031	0.634066
8.11813	5.987071	9.525651	0.634066	13.27904	0.937782
8.11813	5.873177	9.584298	0.69734	13.27904	0.861853
8.11813	5.771938	9.701592	0.570791	13.27904	0.760614
8.11813	5.771938	9.701592	0.570791	13.27904	0.760614

13.57228	0.482208	15.97679	1.08964	19.37831	0.482208
13.63092	0.545482	15.97679	0.975747	19.55425	0.406278
13.68957	0.608756	16.09409	0.798579	19.4956	0.494862
13.80686	0.520172	16.15273	0.74796	19.73019	0.393623
13.92416	0.823888	16.32868	0.558137	19.73019	0.482208
13.92416	0.899818	16.32868	0.456898	19.90613	0.431588
13.92416	0.988402	16.44597	0.570791	19.90613	0.494862
13.92416	1.08964	16.56326	0.659375	20.08207	0.418933
13.98281	1.039021	16.68056	0.520172	20.19936	0.520172
14.04145	0.912473	16.7392	0.469553	20.19936	0.596101
14.04145	0.836543	16.91514	0.418933	20.19936	0.67203
14.04145	0.74796	16.91514	0.494862	20.31665	0.937782
14.1001	0.583446	17.03244	0.431588	20.3753	0.684685
14.15874	0.69734	17.09108	0.507517	20.43395	0.937782
14.15874	0.558137	17.14973	0.482208	20.55124	0.621411
14.21739	0.67203	17.20838	0.558137	20.55124	0.532827
14.33469	0.482208	17.32567	0.494862	20.66854	0.482208
14.39333	0.558137	17.50161	0.456898	20.66854	0.532827
14.51063	0.494862	17.56026	0.494862	20.78583	0.861853
14.51063	0.570791	17.6189	0.646721	20.84447	0.912473
14.62792	0.646721	17.67755	0.596101	20.90312	0.861853
14.62792	0.72265	17.67755	0.659375	21.02041	0.836543
14.62792	0.798579	17.79484	0.646721	21.02041	0.773269
14.62792	0.899818	17.79484	0.74796	21.07906	0.646721
14.74521	0.785924	17.91214	0.634066	21.07906	0.532827
14.8625	1.203534	17.91214	0.520172	21.19636	0.469553
14.8625	1.127605	18.02943	0.621411	21.31365	0.418933
14.8625	1.001057	18.02943	0.418933	21.48959	0.444243
14.92115	0.899818	18.08808	0.520172	21.60688	0.520172
14.9798	0.785924	18.20537	0.418933	21.72418	0.646721
15.09709	0.975747	18.32266	0.456898	21.78282	0.545482
15.03845	0.659375	18.38131	0.380969	21.90012	0.469553
15.15574	0.507517	18.55725	0.469553	22.01741	0.507517
15.21439	0.583446	18.55725	0.380969	22.1347	0.558137
15.39033	0.532827	18.79184	0.456898	22.19335	0.634066
15.44897	0.583446	18.90913	0.393623	22.19335	0.735305
15.56627	0.963092	19.02642	0.469553	22.36929	0.608756
15.68356	0.646721	19.14372	0.520172	22.60388	0.456898
15.74221	0.621411	19.20237	0.608756	22.72117	0.570791
15.80085	0.798579	19.26101	0.684685	22.77982	0.646721
15.8595	0.899818	19.37831	0.596101	22.83846	0.72265
15.97679	1.08964	19.37831	0.482208	22.83846	0.72265

22.89711	0.785924	25.12569	0.380969	29.28961	0.874508
22.89711	0.887163	25.36028	0.444243	29.34825	0.760614
22.89711	1.013712	25.41892	0.494862	29.4069	0.646721
22.95576	1.190879	25.41892	0.558137	29.99337	1.013712
23.01441	1.848932	25.41892	0.621411	30.05202	0.925127
23.01441	1.975481	25.53621	0.558137	30.11066	0.988402
23.01441	2.139994	25.47757	0.608756	30.16931	0.773269
23.01441	2.304507	25.47757	0.709995	30.22796	0.67203
23.1317	4.26601	25.65351	0.545482	30.52119	0.343004
23.19035	4.088842	25.65351	0.634066	30.57984	0.494862
23.19035	3.911674	25.65351	0.545482	30.69713	0.317694
23.1317	3.709196	25.82945	0.596101	30.75578	0.292385
23.19035	3.468754	25.8881	0.709995	30.87307	0.317694
23.36629	3.405479	25.8881	0.798579	31.04901	0.330349
23.36629	2.342471	26.00539	0.608756	31.1663	0.380969
23.42493	2.165304	26.06404	0.507517	31.87006	0.305039
23.42493	2.089374	26.18133	0.545482	31.98736	0.27973
23.54223	1.342738	26.35727	0.583446	32.04601	0.317694
23.54223	1.178225	26.41592	0.608756	32.1633	0.343004
23.60087	1.11495	26.47456	0.684685	32.28059	0.292385
23.77681	2.05141	26.59186	0.684685	32.45654	0.292385
23.89411	2.139994	26.7678	0.596101	32.51518	0.317694
23.89411	2.291852	26.82644	0.69734	32.63247	0.355659
23.89411	2.405746	26.88509	0.823888	32.63247	0.418933
23.89411	2.557604	26.88509	0.912473	32.69112	0.456898
23.89411	2.722117	27.00238	0.912473	32.74976	0.393623
24.0114	2.734772	27.23697	0.507517	32.80841	0.418933
24.07005	1.11495	27.41291	0.545482	32.86706	0.317694
24.12869	1.001057	27.47156	0.583446	32.86706	0.406278
24.30463	1.102295	27.5302	0.469553	32.98436	0.292385
24.30463	1.228844	27.58885	0.406278	33.10165	0.27973
24.36328	1.08964	27.58885	0.482208	33.21894	0.292385
24.36328	1.292118	27.70614	0.393623	33.74676	0.305039
24.48057	1.709728	27.76479	0.355659	33.86406	0.267075
24.48057	1.595835	27.88209	0.368314	33.98135	0.27973
24.53922	1.456631	27.99938	0.418933	34.09864	0.27973
24.65651	1.076986	28.46855	0.431588	34.27458	0.368314
24.65651	0.823888	28.58585	0.380969	34.27458	0.406278
24.71516	0.69734	28.76179	0.355659	34.39188	0.444243
24.71516	0.596101	28.93773	0.368314	34.50917	0.393623
24.83245	0.596101	29.05502	0.406278	34.68511	0.355659
24.83245	0.596101	29.05502	0.406278	34.68511	0.355659

34.74376	0.330349	40.66708	0.2038	46.64904	0.2038
34.97834	0.355659	40.84302	0.241765	46.82499	0.165836
35.15428	0.355659	41.0776	0.22911	47.05957	0.2038
35.27158	0.27973	41.1949	0.2038	47.17686	0.241765
35.44752	0.267075	41.31219	0.216456	47.35281	0.27973
35.50616	0.292385	41.42949	0.241765	47.41145	0.305039
35.62346	0.343004	41.60543	0.216456	47.58739	0.241765
35.62346	0.418933	41.78137	0.191146	47.82198	0.178491
35.74075	0.380969	42.01595	0.178491	48.05657	0.178491
35.91669	0.317694	42.19189	0.178491	48.23251	0.178491
35.97534	0.393623	42.48513	0.2038	48.40845	0.216456
35.97534	0.532827	42.71972	0.2038	48.40845	0.267075
36.09263	0.444243	42.83701	0.25442	48.52574	0.317694
36.20993	0.545482	42.9543	0.2038	48.76033	0.27973
36.26857	0.343004	43.13024	0.191146	48.87762	0.216456
36.44451	0.305039	43.30618	0.241765	49.05357	0.165836
36.56181	0.25442	43.48212	0.241765	49.40545	0.178491
36.79639	0.27973	43.59941	0.2038	49.75732	0.191146
36.97233	0.27973	43.834	0.191146	49.75732	0.2038
37.08963	0.317694	44.06859	0.191146	49.93327	0.178491
37.14827	0.406278	44.18588	0.178491	50.05056	0.178491
37.26557	0.343004	44.47912	0.191146		
37.32421	0.393623	44.7137	0.216456		
37.32421	0.343004	44.77235	0.25442		
37.50015	0.431588	44.77235	0.393623		
37.61745	0.343004	44.88964	0.27973		
37.73474	0.292385	44.88964	0.482208		
37.91068	0.25442	44.94829	0.532827		
38.26256	0.22911	45.00694	0.444243		
38.67309	0.25442	45.00694	0.608756		
38.90768	0.22911	45.12423	0.444243		
39.08362	0.2038	45.24152	0.520172		
39.20091	0.22911	45.41747	0.570791		
39.25956	0.191146	45.41747	0.646721		
39.4355	0.2038	45.53476	0.330349		
39.55279	0.216456	45.7107	0.469553		
39.67008	0.191146	45.7107	0.267075		
39.78738	0.2038	46.06258	0.2038		
40.02196	0.2038	46.23852	0.25442		
40.13926	0.191146	46.41446	0.305039		
40.37384	0.2038	46.41446	0.317694		

C3: X-Ray Diffraction Data for Commercial Na-ZSM-5 Sample Generated Using Dagra Blue Leaf Software (Version 2.0.12.35924)

Table C3: The XRD data for commercial Na-ZSM-5

Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)	Bragg Angle, 2Θ (^{o})	Intensity (Counts)
5.006859	1.465086	8.720079	6.376786	12.5583	1.048941
5.69273	1.406781	8.720079	6.554897	12.65997	0.993315
6.104252	1.40692	8.796336	8.555614	12.78707	1.037886
6.378601	1.407013	9.050523	3.471459	13.04125	1.171555
6.652949	1.34857	9.10136	3.560533	13.14293	1.271778
7.064472	1.465782	9.075941	3.382412	13.80381	1.672752
7.201646	1.641438	9.152197	3.593945	13.82923	1.772948
7.753185	8.464729	9.152197	3.349042	13.98174	1.327721
7.812234	8.826791	9.126779	3.115263	14.00716	1.216411
8.110032	2.814356	9.10136	2.903748	14.82056	2.4412
8.186288	2.669667	9.126779	2.703381	14.84597	2.608188
8.211707	2.346848	9.177615	2.291515	14.92223	1.96256
8.313382	2.2133	9.177615	2.080008	14.94765	1.706535
8.3388	2.16878	9.228453	1.901915	14.99849	1.528441
8.3388	2.22444	9.27929	1.690424	14.99849	1.35033
8.465894	2.402594	9.330128	1.534595	15.02391	1.149963
8.516731	2.614119	9.508059	1.448659	15.10016	0.994141
8.567569	2.881303	9.635152	1.359647	15.151	0.994159
8.567569	3.270921	9.863919	1.448779	15.37977	1.094423
8.592987	3.5047	9.965593	1.337495	15.4306	1.216892
8.592987	3.693943	10.09269	1.226218	15.60854	1.395064
8.592987	3.860923	10.42313	1.181802	15.63395	1.484128
8.643824	4.02792	10.5248	1.148441	15.58312	1.628826
8.643824	4.217163	10.60106	1.17073	15.60854	1.595439
8.618404	4.417528	10.75357	1.137387	15.73563	1.450766
8.618404	4.573376	10.82983	1.181939	15.8373	1.428536
8.618404	4.729223	10.95692	1.081795	15.88814	1.640061
8.643824	4.94074	11.00776	1.12634	15.93898	1.81819
8.669242	5.207915	11.18569	1.093004	15.98981	1.996319
8.669242	5.419421	11.3382	1.081924	16.04065	1.873883
8.694661	5.530749	11.51613	1.104248	16.04065	1.651244
8.694661	5.686596	11.64323	1.126555	16.09149	1.495414
8.694661	5.864708	11.77032	1.171126	16.14233	1.317321
8.694661	6.042819	11.84657	1.271339	16.80321	0.816607
8.720079	6.209806	11.89741	1.226829	16.93031	0.749858
8.720079	6.376786	12.5583	1.048941	16.93031	0.749858

17.26075	0.783366	21.87872	0.662477	26.45408	0.824667
17.31159	0.827911	21.87872	0.729269	26.4795	0.891466
17.41326	0.783417	21.9804	0.71817	26.58117	1.036217
17.41326	0.861341	22.10749	0.829534	26.58117	1.147536
17.48952	0.894763	22.15833	0.963134	26.60659	1.203204
17.56577	0.883656	22.26	0.829585	26.70827	1.069655
17.64203	1.006134	22.31084	0.996581	26.73368	1.169851
17.61661	1.117445	22.89547	2.187898	26.83536	1.125357
17.69287	1.184261	22.89547	2.521857	26.96245	1.214456
17.71828	1.262194	22.94631	2.366027	27.03871	1.080899
17.79454	1.162033	22.94631	5.828062	27.62334	0.580159
17.81996	1.239964	22.97173	6.017313	27.75043	0.502278
17.94705	1.150952	23.02256	6.273365	27.92836	0.491207
17.97247	1.095301	23.20049	8.00695	28.00462	0.546892
18.04873	0.972875	23.40384	5.624782	28.13171	0.602595
18.88754	0.705993	23.40384	5.335351	28.28423	0.591515
18.9638	0.66149	23.81054	3.198155	28.41132	0.647217
19.01464	0.717167	23.81054	3.064572	28.46215	0.547047
19.11631	0.694938	23.91222	3.242717	28.58925	0.469166
19.19257	0.839679	23.96305	3.565561	28.76718	0.446963
19.98054	0.695231	23.93764	3.821588	28.91969	0.447014
20.10764	0.717537	23.93764	4.021963	29.02136	0.5695
20.15847	0.773214	24.03931	4.099921	29.02136	0.547236
20.23473	0.862296	24.01389	3.843878	29.09762	0.658582
20.28557	0.895709	24.01389	3.509919	29.12304	0.614063
20.73488	1.029444	24.06473	3.008998	29.93644	1.259991
20.78572	1.296628	24.11557	2.563737	29.98727	1.3268
20.81114	1.497011	24.87812	0.768473	30.08895	1.19325
20.91282	1.318935	25.05606	0.568159	30.16521	1.015166
20.96365	1.508196	25.20857	0.579342	30.24146	0.859344
20.96365	1.118578	25.33566	0.568253	30.26688	0.881616
20.96365	0.940467	25.43733	0.690738	30.36856	0.859388
21.06532	1.241063	25.56443	0.802101	30.36856	0.926179
21.06532	0.728993	25.74236	0.802162	30.5719	0.570025
21.11616	0.651087	25.89487	1.01372	30.64816	0.458731
21.167	0.695632	25.94571	1.147321	30.85151	0.369745
21.21784	0.606594	25.94571	0.91355	30.87693	0.458808
21.37035	0.528721	26.04738	0.813397	31.02944	0.436596
21.54828	0.584442	26.1999	0.746657	31.10569	0.492282
21.67537	0.684672	26.30157	0.780087	31.13111	0.54795
21.80247	0.71811	26.40324	0.757858	31.18195	0.536836
21.87872	0.662477	26.45408	0.824667	31.94451	0.34785

31.94451	0.34785	35.61198	0.415882	43.92388	0.229453
31.94451	0.425773	35.66282	0.493824	44.2289	0.240687
32.09702	0.414693	35.78991	0.538395	44.94062	0.908845
32.30037	0.370235	35.81533	0.482743	45.01688	0.830948
32.4783	0.437087	35.86617	0.549552	45.0423	0.942276
32.6054	0.503921	35.917	0.594098	45.11856	0.830983
32.65623	0.51507	35.96784	0.571851	45.24565	0.68631
32.70707	0.637539	36.0441	0.627537	45.29649	0.719723
32.73249	0.503964	37.03543	0.416365	45.83028	0.285758
32.75791	0.65982	37.51838	0.550112	46.00821	0.252422
32.78333	0.503981	37.62005	0.461091	46.1353	0.285861
32.83416	0.659846	37.72173	0.360937	46.21156	0.285886
32.91042	0.53742	37.8234	0.305312	46.23698	0.341555
32.91042	0.526288	38.00134	0.271976	46.36407	0.319334
32.96126	0.359327	38.20469	0.272046	46.36407	0.374994
32.96126	0.459514	38.78931	0.272243	46.49117	0.319378
33.13919	0.359387	38.76389	0.350158	46.41491	0.43067
33.24086	0.292629	39.0435	0.261197	46.61826	0.308289
33.24086	0.381685	39.27227	0.239011	46.79619	0.185896
33.41879	0.337218	39.47562	0.239079	46.9487	0.230477
33.44421	0.437413	39.83147	0.294859	46.99953	0.263889
33.54588	0.381789	40.00941	0.250392	47.10121	0.208264
33.54588	0.459712	40.36527	0.283908	47.12663	0.297328
33.64756	0.326163	40.61945	0.250598	47.22831	0.286231
34.0106	0.359682	40.72113	0.284029	47.25372	0.364163
34.06144	0.415358	40.9499	0.261842	47.40623	0.319686
34.1377	0.44878	41.15325	0.284175	47.40623	0.408742
34.26479	0.459955	41.33118	0.273103	47.43166	0.419883
34.36646	0.537914	41.61078	0.306594	47.58417	0.330879
34.39188	0.615846	41.78871	0.262126	47.71126	0.241866
34.49356	0.582485	41.94122	0.295574	47.88919	0.219663
34.5444	0.460049	42.09374	0.217701	48.01628	0.208574
34.5444	0.526841	42.80546	0.251338	48.82968	0.320169
34.72233	0.493506	42.90713	0.295901	48.95677	0.264552
34.69691	0.571421	43.08506	0.273696	49.16012	0.208961
34.84942	0.471285	43.18674	0.307127	49.36347	0.264689
34.84942	0.560341	43.28841	0.273765	49.5414	0.309278
34.9511	0.437923	43.31383	0.329434	49.71933	0.275941
35.12903	0.426851	43.44093	0.262685	49.82101	0.331636
35.33237	0.304469	43.44093	0.318345	49.87185	0.242598