Synthesis of Zeolites from Bolivian Raw Materials for Catalysis and Detergency Applications

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ABSTRACT

Zeolites are very useful in many technological applications such as catalysis, separation and purification of gases and solvents, ion-exchange, etc. The production of zeolites is nowadays carried out with a variety of reagents, such starting materials render large scale production of zeolites expensive. Hence alternative synthesis routes for zeolite production at a lower cost are currently under investigation. One of these routes involves the use of natural aluminosilicate raw materials which have many advantages such as their availability, low price, workability, etc.

The aim of the present work was to provide routes to produce synthetic zeolites of industrial attractiveness derived from non-expensive Bolivian raw materials like clays and diatomites. In particular, the work was focused on the synthesis of intermediate- and low-silica zeolites: zeolite Y and zeolite A. The raw materials as well as intermediate materials and final zeolite products were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen gas adsorption, inductively coupled plasma mass spectrometry (ICP-SFMS), and UV-VIS spectroscopy.

The first part of the study addressed the synthesis and characterization of intermediate silica zeolite Y from diatomite. Prior to synthesis, the diatomite was leached in sulfuric acid to remove impurities, but this step also resulted in dealumination. Therefore, aluminum sulfate was used as an extra source of aluminum. The raw materials were reacted hydrothermally at 373 K in aqueous medium with sodium hydroxide. Variations in parameters like the Na$_2$O/SiO$_2$ ratio and synthesis time were investigated. As a result, micro-sized crystals of zeolite Y were obtained. It was possible to achieve high zeolite yield at a Na$_2$O/SiO$_2$ ratio of 0.9, which produced zeolite Y with a SiO$_2$/Al$_2$O$_3$ ratio of 3.9. Also, synthesis of almost pure zeolite Y with a SiO$_2$/Al$_2$O$_3$ ratio of 5.3 in low yield at a Na$_2$O/SiO$_2$ ratio of 0.6 was achieved. In this respect, diatomite behaved similarly to colloidal silica in traditional syntheses, with both sources of silica having a high degree of polymerization. Zeolite Y with the latter SiO$_2$/Al$_2$O$_3$ ratio might be useful for the production of ultra-stable zeolite Y for use as FCC catalyst.

A similar acid leaching procedure, this time with hydrochloric acid, was used for dealumination of diatomite to increase the SiO$_2$/Al$_2$O$_3$ ratio and to reduce the amount of iron and other impurities for synthesis of high silica ZSM-5 zeolite. This procedure was successful
in producing well-crystallized ZSM-5 from diatomite in combination with sodium hydroxide and n-butyl amine under appropriate synthesis conditions.

The second part of this study dealt with the synthesis of low silica zeolite A from Bolivian montmorillonite-type clay. This clay did contain significant amounts of quartz. Hence, an alkali fusion treatment was applied to the clay by fusing the clay at high temperature with NaOH to make the material more reactive and to take advantage of all the silica present in the clay. The raw clay had a SiO$_2$/Al$_2$O$_3$ ratio of 4, and sodium aluminate was added to the mixture to decrease this ratio to 2. An optimization of the synthesis time was performed. The final zeolite product exhibited high brightness despite the presence of iron in appreciable amount in the starting material and the final product. This was attributed to the magnesium in the raw material, which exerted a masking effect on iron. The latter was incorporated into extraneous magnesium aluminosilica compounds, thereby increasing brightness and strongly decreasing the overall yellowness. This simple method appears as a promising alternative to the complex and costly techniques suggested to reduce the iron content in natural raw materials, especially kaolin.

To summarize, this work reports the synthesis of zeolites with promising characteristics from Bolivian raw materials. However, further optimization is required to qualify these products for industrial applications. Moreover, this study might help in the development of poor regions of the Bolivian Altiplano and open up for large scale production, since the methods developed in this work are simple and non-expensive.
ACKNOWLEDGMENTS

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LIST OF PAPERS

This thesis is based on the following papers, referred to in the text by Roman number.

I. Synthesis of zeolite Y from diatomite as silica source

Gustavo García, Saúl Cabrera, Jonas Hedlund, Johanne Mouzon

Submitted to Journal of Microporous and Mesoporous Materials

II. Preparation of zeolite A with excellent optical properties from clay

Gustavo García, Wilson Aguilar-Mamani, Ivan Carabante, Saúl Cabrera, Jonas Hedlund,

Johanne Mouzon

Submitted to Journal of Alloys and Compounds

III. Synthesis of ZSM-5 from inexpensive raw materials

Wilson Aguilar-Mamani, Gustavo García, Jonas Hedlund, Johanne Mouzon

Submitted to SpringerPlus
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APPENDED PAPERS
1. INTRODUCTION

1.1. General

A zeolite is an inorganic crystalline aluminosilicate with a network of pores. These aluminosilicates are composed of three-dimensional frameworks of \( \text{SiO}_4^4- \) and \( \text{AlO}_4^5- \) tetrahedrons which share corners through oxygen atoms and form open structures; zeolites network possess an overall negative charge which is balanced by cations which can move freely in or out this framework. An empirical formula representative of a zeolite can be expressed in the following way:

\[
M_{x/n} \left[ (\text{AlO}_2)_{x} (\text{SiO}_2)_{y} \right] \cdot w\text{H}_2\text{O}
\]

where \( M \) is an extra-framework cation (alkaline or alkaline earth metal) of valence \( n; \) \( y/x \) represents the Si/Al ratio of the zeolite and \( w \) is the number of water molecules.

Zeolites are classified according to their structural differences and assigned to established structures that satisfy the rules of the IZA Structure Commission i.e. for zeolite A, LTA Linde Type A (Linde Division, Union Carbide); for zeolite X and Y, FAU (Faujasite) and MFI for the ZSM – 5, etc. One structural difference is the size of the pore openings that can vary in the micropore range of ~2 to 13 Å. Factors influencing the size of the pores are the location, coordination and size of the extra-framework cations, i.e. Na\(^+\) replacement by either K\(^+\) or Ca\(^{2+}\) cations causes a decrease or an increase of pore aperture in zeolite A, respectively.

The factors determining the physical and chemical properties of zeolites are exerted by the Si/Al ratio, the interconnected framework of micropores at a molecular scale and the compensating cations. The acidity of the zeolite is defined by the Si/Al ratio, a low ratio causes the surface to become more hydrophilic (having a strong affinity for water) and confers to zeolite acid sites (Bronsted acid and Lewis acid) that results from the net negative framework charge. The channels and cavities of zeolite frameworks provide both high surface area and shape selectivity, which is defined as mass transfer effect excluding certain reactant molecules based on size relative to the zeolite pore window size. All these properties renders zeolites versatile as heterogeneous catalysts [1].
1.2. Zeolites of particular interest

There are three main uses for zeolites in industry, the most important being catalysis, but others include gas separation and ion exchange. Moreover, their use is becoming important in many environmental applications like removal of heavy metals, treatment of radioactive species or organic pollutants and water purification, as well as other applications areas such as agriculture and medicine, etc.

Three well known and industrially important zeolites may be classified into three groups according to the Si/Al ratio in their frameworks as low, medium and high silica zeolites:

- **Zeolite A (LTA)** (Figure 1.1A) defined by a Si/Al ratio of 1, is a low silica zeolite represented by the following formula: \( \text{Na}_{12} \left[ (\text{AlO}_2)_{12} (\text{SiO}_2)_{12} \right] \cdot 27\text{H}_2\text{O} \). The crystal structure is cubic with a lattice parameter of 12.32 Å. Zeolite A is characterized by a 3-dimensional network consisting of cavities of 11.4 Å in diameter separated by circular openings of 4.2 Å in diameter [2].

- **Faujasite type zeolites (FAU)** (Figure 1.1B) defined by a medium Si/Al ratio between 1-1.5 for zeolite X and greater than 3 for zeolite Y [3]. The basic structural units for this type of zeolite are sodalite cages which form supercages able to accommodate spheres up to 1.2 nm in diameter. The structure is composed of equidimensional channels perpendicularly intersected. The openings to these large cavities are 12-membered oxygen rings with a free diameter of 7.4 Å.

- **ZSM-5 (MFI)** (Figure 1.1C), a high silica zeolite, belongs to the pentasil family. It can be synthesized in a wide range of Si/Al varying from 5 to infinity. The structure is composed of a three dimensional pore system consisting of sinusoidal channels (5.1x5.5 Å) and straight channels (5.3x5.6 Å) [4].
Figure 1.1. Zeolite structures, silicon and aluminium atoms are placed at the vertices and connected by lines: (A) Zeolite A, the sodalite cages are linked to each other via double four-membered rings forming the larger cage [5]; (B) FAU-type, the sodalite cages are connected via double six-membered rings; (C) ZSM-5, composed of a three dimensional pore system of sinusoidal channels and straight channels.

1.3. Zeolites in adsorption and catalysis

Zeolites are extremely useful as catalysts for several important reactions involving organic molecules, they have found their place in a number of applications for the production of petrochemicals, often replacing environmentally unfriendly catalysts. Zeolite catalysts typically yield fewer impurities, have higher capacity, give greater unit efficiency, and afford higher selectivity. Unlike the more hazardous acid catalysts that have been used in the past, e.g., phosphoric acid, hydrofluoric acid, etc., zeolites are non-hazardous and can be regenerated [6]. FAU (Y) and MFI (ZSM-5) zeolites are extensively used in petroleum refining and petrochemicals production either as catalysts or adsorbents, i.e., Fluid Catalytic Cracking (FCC), aromatics alkylation, natural gas dehydration and separation media. Both zeolites can act as shape selective catalysts due to their ability to promote a diverse range of catalytic reactions including acid (zeolites in their H⁺ form) and metal induced reactions (zeolites can be used to support active metals). The shape selective reactions occur within the pores of the zeolite, which allows a greater degree of product control by limiting the formation of products larger than the pore size of the zeolite [7].

Zeolite Y, with a framework topology like that of zeolite X and the rare zeolite mineral faujasite, has a higher stability (acid and thermal) over the more aluminous zeolite X. The differences between zeolite X and Y in terms of composition and structure were found to have a striking and unpredicted effect on the properties, making zeolites Y based catalysts valuable in many important catalytic applications involving hydrocarbon conversion. Hence, zeolite Y
is the most widely employed zeolite catalyst due to its use in the FCC process for the conversion of heavy petroleum molecules into gasoline-range hydrocarbons because of its high selectivity, high concentration of active acid sites, and thermal stability [8-10].

Zeolite ZSM-5 is widely used in catalytic applications as catalysts for diverse petrochemical processes [11, 12]. Performance of ZSM-5 as a catalyst depends on three primary factors: (i) acidity (nature, strength and density), (ii) crystal size, which affects the intra-crystalline diffusion of reactant molecules, and (iii) crystal morphology, which might govern the exposure of a particular plane towards the reactant molecules [13]. The properties of ZSM-5 stated above allow this material to be used as a FCC catalyst additive for boosting gasoline octane number. ZSM-5 zeolite is also an efficient catalyst for catalytic degradation of polyolefin because of its strong acidity for the carbon-carbon bond scission and unique pore structure to reduce coke formation [14].

1.4. Zeolites in detergency applications

Zeolites A and X are the most common commercial adsorbents. Both zeolites are nearly "saturated" in aluminum in the framework composition with a molar ratio of Si/Al ≈ 1, which is the highest aluminum content possible in tetrahedral aluminosilicate frameworks and Lowenstein's rule is obeyed and no Al-O-Al bridges occur. As a consequence, they contain the maximum number of cation exchange sites balancing the framework aluminum, and thus the highest cation contents and exchange capacities. This property confers to zeolite A water softening abilities by ion exchanging Ca^{2+} and to a lesser extent Mg^{2+} for Na^{+}, thereby preventing precipitation of calcium compounds [15]. Therefore, the most important industrial applications of zeolite A is as detergent builder [16, 17].

There are various requirements set on a zeolite to be used as a detergent grade builder, e.g. the size of the particles, crystal shape, brightness and cation exchange capacity (CEC). The optimal range for particle size is in between 1-10 µm [18] to avoid particle retention in textile fibers and prevent unacceptable deposition of particles in textile materials, fabric and machine parts [19]. Besides, an appropriate morphology of the crystals helps to avoid incrustation; sharp edges in zeolite A crystals can be easily entangled in textile fibers and, on the other hand, zeolite A with rounded corners and edges tend to decrease incrustation on textile materials. Brightness is another important property of a detergent builder; it has to be at least 90% of the ISO reflectance measured on BaSO₄ or MgO. Finally, the CEC of detergent
builders must be as high as possible with 510 meqCa\(^{2+}\)/100g of anhydrous solid being a recommended minimum [20] and 592 meqCa\(^{2+}\)/100g the highest achievable value at 294 K in a 1000 ppm solution of CaCl\(_2\) [21].

The properties of zeolite A produced from kaolin in terms of CEC, particle size and morphology were found to be adequate for use as detergent builder. However problems associated with brightness and yellowness and related to the iron content are usually encountered when using kaolin for zeolite production [22, 23]. Various techniques for removal of iron were investigated [24] such as selective flocculation [25, 26], magnetic separation [27, 28], acid leaching [29, 30], optimum temperature for metakaolinization [17] and chemical treatments [31]. As an example, Chandrasekhar [24] managed to reduce the amount of Fe\(_2\)O\(_3\) in the final zeolite product from 0.59% to 0.04% starting with a Chinese kaolin containing 0.69 % Fe\(_2\)O\(_3\) by a combination of treatments, i.e. clay refining, control of alkali concentration, complexing and washing with alkaline water. Dramatic improvement of the color properties of the final zeolite A were reported, the brightness increased from 72.9 to 81.7% and yellowness reduced from 11.5% to 7.8%. Nevertheless, these separation procedures represent additional costs to the general process.

1.5. Zeolite synthesis

The synthesis of zeolites involves many variables which define the nature of the final product. Generally, the method of zeolite production involves dissolving an aluminum source (metal or oxide) in alkali media. A silica source (and a template if required) is added to the initial solution, forming a slurry that is stirred until a homogeneous gel forms. After an induction time called aging time, the gel is transferred to an autoclave and usually heated to temperatures in the range of 353-473 K for a synthesis time varying from hours to days depending on the zeolite desired. Most of the zeolites can be obtained at temperatures < 373 K. However, in order to reduce synthesis time and control the size of the crystals, thermal treatments are often performed at temperatures > 373 K. Also, additional treatments were reported to improve the synthesis of zeolites from natural raw materials by using acid treatment and/or alkali fusion steps. The properties of the starting materials used in the reaction mixture are of great importance and influence the properties of the resulting material. The role of each of the aforementioned reactants is summarized in the following table:
Table 1.1. Chemical sources and their function in zeolite synthesis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_4$^-</td>
<td>Primary building unit(s) of the framework</td>
</tr>
<tr>
<td>AlO$_4$^-</td>
<td>Charge difference origin in the framework</td>
</tr>
<tr>
<td>OH^-</td>
<td>Mineralizer and provider of basic media</td>
</tr>
<tr>
<td>M (alkali cation), template</td>
<td>Counter-ion of framework charge, guest molecule, pore stabilizer</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Solvent, guest molecule inside the framework</td>
</tr>
</tbody>
</table>

Pure chemical grade reagents are mostly used to produce materials which fulfill all the aforementioned requirements. Concerns about energy consumption, carbon economy and production costs have called the attention of researchers to seek cheaper raw materials for zeolite synthesis [32, 33]. Many studies have been published on the synthesis of zeolite A from raw materials such as kaolin, diatomite, bentonite, fly ash, or smectite [34-38]. Kaolin is of particular interest because it possesses the appropriate SiO$_2$/Al$_2$O$_3$ ratio that matches the composition of zeolite A [39]. However, kaolin must be activated by calcination at high temperature to produce an amorphous material called metakaolin that can be easily digested during zeolite synthesis. Therefore, calcination is usually carried out in the temperature range of 773-1273K [40] in order to convert kaolin to metakaolin.

An attractive raw material with high silica content is diatomite, a type of siliceous biologic sedimentary rock. It contains mainly amorphous silicon oxide derived from biogenic siliceous sediments (unicellular algae skeletons, frustules) and is available in bulk quantities at low cost [41]. Being amorphous and silica rich, diatomite does not require any additional heat treatment or silica source for use in the synthesis of FAU-type zeolites, both of which representing additional costs [42]. However, the occurrence of CaCO$_3$ and Fe as impurities is quite common in diatomite type materials [43] and adequate treatments must be employed for purification [44]. Moreover, potassium, which is known to promote the formation of zeolite P [45], is also common in this kind of raw material meaning that a reduction in potassium content is required.

Another interesting raw material rich in Si and Al is montmorillonite, a well-known clay mineral in the sub-group of dioctahedral smectites. This natural aluminosilicate clay is a 2:1
phyllosilicate and has a sheet-type structure. There exist charge deficiencies originated by different Si$^{4+}$ substitutions by Al$^{3+}$ cations placed in-between the laminar environment that allows the insertion of alkaline cations, alkaline earth cations and water [46]. However, natural clays of this type usually contain quartz and do not produce a reactive product such as metakaolin upon calcination. The energy used for the metakaolinization heat treatment can be used with advantage to fuse raw materials containing quartz under the action of the sodium required for zeolite synthesis. It is known that through alkali activation large amounts of aluminosilicates can be transformed into more soluble species [47].

All these types of natural raw materials can be found in huge quantities and can be mined to a low cost in many areas in Bolivia.

1.6. Scope of the present work

This study aimed at developing methods for the synthesis of zeolites from Bolivian raw materials, i.e. intermediate silica FAU-type zeolites and high silica ZSM-5 from diatomaceous earth and low silica zeolite A from a montmorillonite-clay.

The present study also aimed of assessing the characteristics of the final zeolite products i.e. Si/Al ratio, crystallinity, ion exchange capacity, brightness, crystal sizes, etc. These properties are of great importance in the intended applications such as in catalysis and/or as detergent builder.
2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Zeolite Y synthesis

Diatomite originating from the Murmuntani zone, near Llica in the Potosi region of Bolivia was used as an aluminosilicate source for zeolite Y synthesis. Sulfuric acid (Merk, pro analysis 98 %) was used to remove impurities from diatomite. Aluminum sulfate octadecahydrate (Al₂(SO₄)₃ * 18H₂O, Riedel-de Haën, p.a., > 99%) was employed to adjust the SiO₂/Al₂O₃ ratio to that of typical syntheses of zeolite Y. The alkalinity of the synthesis mixture was regulated with sodium hydroxide (NaOH, Sigma Aldrich, p.a., ≥ 98%). Silicon (Merck, p.a., >99) was used to calibrate the peak position during XRD experiments. Zeolite Y (Akzo Nobel, CBV100L-T) was used as a reference sample.

2.1.2. ZSM-5 synthesis

For synthesis of ZSM-5, the aforementioned diatomite was used as the aluminosilicate source. Hydrochloric acid (Merk, pro analysis 37 %) was used for the acid treatment of the diatomite to remove impurities and to increase SiO₂/Al₂O₃ ratio. Sodium hydroxide (SiO₂/Al₂O₃) was used as a mineralizing agent, n-butylamine (NBA, Sigma Aldrich, 99.5 %) was used as an organic template.

2.1.3. Zeolite A synthesis

Montmorillonite-type clay (RMA) sampled from the Rio Mulatos zone (Potosi, Bolivia) and commercial kaolin (Riedel-de-Haën, pro analysis) were used as aluminosilica sources for zeolite A synthesis. Sodium hydroxide (NaOH, Sigma Aldrich, p.a., ≥ 98%) was used for alkali fusion. Sodium aluminate anhydrous (NaAlO₂, Riedel-de Haën, p.a., Al₂O₃ 50 – 56 %, Na₂O 40-45 %) was used to adjust the SiO₂/Al₂O₃ ratio to that of typical synthesis of zeolite A. Calcium nitrate (Ca(NO₃)₂*4H₂O, Merck) and magnesium nitrate (Mg(NO₃)₂*6H₂O, Merck) were utilized to investigate the influence of Ca and Mg on the color properties of alkali-activated kaolin. Sodium nitrate (NaNO₃, Merck) was utilized for ion exchange. Commercial zeolite A (Akzo Nobel) powder was used as a standard. Barium sulfate (BaSO₄, Sigma Aldrich, p.a. 99%) was used as a standard for brightness and yellowness measurements.
2.2. Synthesis procedures

A schematic description of the synthesis procedures is depicted in Figure 2.1.

![Schematic diagram of synthesis procedures](image)

**Figure 2.1.** Schematic representation showing the various treatment carried out for the production of each zeolite.

### 2.2.1. Zeolite Y

The raw diatomite (DA) was crushed and treated with 6M H₂SO₄ at 373 K for 24 hours in an autoclave under hydrothermal conditions, rinsed with distilled water until the pH in the filtrate was close to 7 and dried overnight. Acid treated diatomite (aDA) as well as a suitable amount of Al₂(SO₄)₃, were added to NaOH solutions of different concentrations whilst stirring. The molar ratios of the synthesis mixtures were: \( \text{Na}_2\text{O}/\text{SiO}_2 = 0.4 – 2.0; \text{SiO}_2/\text{Al}_2\text{O}_3 = 11; \)
H₂O/Na₂O = 40. These solutions were aged with stirring at room temperature in glass beakers for 24 hours, then the reaction mixture was transferred to Teflon-lined autoclaves and placed in an oven at 373 K for different periods of time and subsequently quenched in cold water. The solid product was separated from the reaction mixture by suction filtering using filter paper grade 00H and repeatedly filtered and dispersed in distilled water until the pH of the filtrate liquid was 9. The final solid product was dried in an oven at 373 K overnight and weighed to estimate the yield. Samples were denoted according to the Na₂O/SiO₂ used and the synthesis time e.g S0.6-24h corresponds to a sample obtained from a mixture with a molar Na₂O/SiO₂ ratio of 0.6 after 24 h of synthesis. A schematic description is shown in Figure 2.1.

2.2.2. ZSM-5

The raw diatomite was stirred in hydrochloric acid for 150 minutes at 388 K. Subsequently, the suspension was quenched and the acid leached product was filtered and washed with distilled water until the pH value was close to 7. The synthesis mixtures were prepared by mixing the aluminosilicate sources with distilled water, NBA and sodium hydroxide. The molar ratio in the synthesis mixtures were: Na₂O/SiO₂ = 0.18; SiO₂/Al₂O₃ = 33; SiO₂/NBA = 7; H₂O/SiO₂ = 30. The mixture was aged under stirring for 24 hours at room temperature and was thereafter hydrothermally heated in Teflon lined stainless steel autoclaves kept for different times in an oil bath at 438 K. After hydrothermal treatment, the solids were recovered by filtration and washed with distilled water until the pH reached a value close to 8. Drying at 373 K overnight and finally calcination at 823 K for 6 hours to remove the template were applied (see Figure 2.1).

2.2.3. Zeolite A

RMA clay was added to sodium aluminate and sodium hydroxide in calculated amounts to set both the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios to 2. The mixture was meticulously crushed in an agate mortar until a homogeneous powder was obtained. The crushed powder was placed in nickel crucibles and heated at 873K for 1 hour at a heating rate of 10 K/min. The resultant mixture was crushed again, dispersed in distilled water and aged whilst stirring for 6 h. In the case of kaolin (KFA), the same procedure was used without the addition of sodium aluminate. The molar ratio of the components in the mixtures was SiO₂/Al₂O₃ = X, Na₂O/SiO₂ = 2 and H₂O/Na₂O = 40 with X varying between 2.0 and 1.15. After the aging period, the reaction mixture was transferred to Teflon-lined autoclaves and heated at 373 K for different times in
order to perform an optimization of the hydrothermal treatment. Subsequently, the autoclave
was quenched in cold water and the solid products were filtered and washed in distilled water
until the pH in the filtrate liquid reached 9 and thereafter dried at 373 K overnight. The
prepared samples were denoted according to the clay that was used, namely RMA or KFA,
followed with the molar SiO$_2$/Al$_2$O$_3$ ratio into brackets and synthesis time, e.g. RMA(2.0)-3h
corresponds to a sample obtained from a mixture with a molar SiO$_2$/Al$_2$O$_3$ ratio of 2.0 using
Rio Mulatos clay after 3 h synthesis (see Figure 2.1).

2.3. Characterization

To determine the chemical composition of the raw materials and final products, inductively
coupled plasma – sector field mass spectrometry (ICP-SFMS) analysis was carried out. The
morphology of the raw materials, intermediate products and final products were studied by
extreme high resolution-scanning electron microscopy using a XHR-SEM Magellan 400
instrument. The samples were investigated using a low accelerating voltage and no conductive
coating was used. Nitrogen adsorption data at 77 K was recorded using a Micromeritics
ASAP 2010 instrument. Specific surface area was determined by using the Brunauer–
Emmett–Teller (BET) method. The micropore volume of the final products was determined
by the $t$-plot method using the formula:

$$t = \frac{13.9900}{(0.0340 - \log(P/P_0))}^{0.5000}$$

The mineralogical composition of the raw materials and final products were determined by
X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer, equipped with
a PixCel3D detector and a graphite monochromator. CuK$\alpha_1$ radiation with $\lambda = 1.540598$ Å at
45 kV and 40 mA was used in the 20 range 5-50° at a scanning speed of 0.026°/s. The
diffractionograms were compared with the powder diffraction files (PDF) database. The
SiO$_2$/Al$_2$O$_3$ ratio of the FAU zeolites was calculated by assessing the lattice parameter from
the (555) reflection of faujasite and using the empirical relationship proposed by Rüscher et
al. [48]:

$$x = 5.348a_0 – 12.898$$

with $x$ = Al molar fraction and $a_0 = the length of the unit cell or lattice paremeter (Å).

Crystallinity of the zeolite products was assessed by calculating the area under the peaks in
the 2Ω region after background removal and comparing it to that reported for commercial
zeolite powders; for zeolite Y, the peaks in the 2θ region 31.0° – 32.5° were used; for ZSM-5 the peaks in the 2θ region 22.0° – 25.0° and for zeolite A in the 2θ region 6.5° – 7.5°. The following formula was used:

\[
X-ray\ crystallinity\ (%) = \left( \frac{\sum \text{Area peaks sample}}{\sum \text{Area peaks standard}} \right) \times 100
\]

Energy dispersive spectroscopy (EDS, X-max detector 50 mm², Oxford Instruments) was also performed to establish the overall composition of the final products (individual crystals and extraneous phases). EDS was carried out at 10 kV using a SEM equipped with a microinjector (Merlin SEM, Carl Zeiss) in order to mitigate charging by blowing nitrogen gas close to the surface of samples. The concentration of Na, Mg, Al and Si was measured by scanning a large area (by using a low magnification of 100 times) to avoid diffusion of Na, while the concentration of Ca was measured locally in 10 individual crystals. Brightness and yellowness were measured on a UV/VIS spectrometer equipped with an integrating sphere (Perkin Elmer Lambda 2SUV/VIS) and expressed in percentage of the reflectance obtained on Ba₂SO₄ [49]. Brightness was measured at 457 nm, while the difference between the reflectance measured at 570 and 457 nm yielded a measure for yellowness. The number of equivalents-gram was calculated for Ca²⁺ in each case. The total exchange equivalents for Ca²⁺ was assessed by calculating the number of equivalents of Ca²⁺ after the exchanged process subtracted by the number of equivalents of Ca²⁺ present in the zeolite before ion exchange.
3. RESULTS AND DISCUSSION

3.1. Syntheses from Bolivian diatomite (Paper I and III)

3.1.1. Zeolite Y (Paper I)

The work described in Paper I focusses on the synthesis of zeolite Y from diatomite with a high degree of crystallinity.

3.1.1.1. Starting materials

The XRD diffractogram of the raw diatomite (Figure 3.1) indicates the presence of halite (NaCl), calcite (CaCO₃), quartz and amorphous silica as main components, as well as muscovite and albite as secondary components, which is typical of diatomites of this type [50]. Since the raw material originates from a region near the Uyuni salt lake, the presence of sodium chloride is expected; the composition of the original diatomite obtained by ICP-SFMS is given in Table 3.1. The main elements in raw diatomite (DA) are silicon and aluminum, but Fe, Na, Ca, K and Mg remained as minor impurities.

![XRD diffractograms of (a) raw diatomite DA, (b) acid treated diatomite aDA.](image_url)
Table 3.1. Chemical composition of raw diatomite (DA) and the acid treated diatomite (aDA) determined by ICP-SFMS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (%)</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>DA</td>
<td>61.58</td>
<td>6.94</td>
</tr>
<tr>
<td>aDA</td>
<td>94.45</td>
<td>3.51</td>
</tr>
</tbody>
</table>

After leaching, only quartz, minor components (muscovite and albite) and calcium were still present in appreciable amounts as shown by the comparison between the XRD (Figure 3.1) and ICP-SFMS results (Table 3.1) of the original material and the acid treated diatomite. Sodium (and potassium) chloride was removed by rinsing and the content of the major impurities was considerably reduced by the leaching treatment. However, the SiO₂/Al₂O₃ ratio was increased from 15 to 46.

3.1.1.2. Synthesis optimization

In order to optimize the synthesis of zeolite Y, different compositions were investigated at fixed aging and synthesis temperatures and times. The Na₂O/SiO₂ ratio was varied in the range 0.4-2.0 in our system using diatomite as starting material, see Table 3.2.
**Table 3.2.** Composition and synthesis conditions for samples S0.4 to S2.0.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Na$_2$O/SiO$_2$</th>
<th>H$_2$O/Na$_2$O</th>
<th>Ageing Time (h)</th>
<th>Temperature (K)</th>
<th>Heating Time (h)</th>
<th>Temperature (K)</th>
<th>Main product (secondary product within brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2.0</td>
<td>11.6</td>
<td>2.0</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S1.2</td>
<td>11.1</td>
<td>1.2</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.9</td>
<td>11.1</td>
<td>0.9</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.8</td>
<td>11.1</td>
<td>0.8</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.7</td>
<td>11.1</td>
<td>0.7</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.6</td>
<td>11.6</td>
<td>0.6</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.5</td>
<td>11.6</td>
<td>0.5</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
<tr>
<td>S0.4</td>
<td>11.5</td>
<td>0.4</td>
<td></td>
<td>40</td>
<td>24</td>
<td>298</td>
<td>48</td>
<td>373</td>
</tr>
</tbody>
</table>

**Figure 3.2.** SiO$_2$ – Al$_2$O$_3$ – Na$_2$O phase diagram showing the distribution of the samples synthesized at different Na$_2$O/ SiO$_2$ ratios and the regions where zeolite Y is produced depending on the silica source.
Breck and Flanigen [3] identified two different compositional regions in the SiO$_2$-Al$_2$O$_3$-Na$_2$O phase diagram (Figure 3.2) depending on whether sodium silicate or colloidal silica was used as silica source. In the same diagram, the compositions of our synthesis mixtures are indicated. The Na$_2$O/SiO$_2$ ratio was varied in the range 0.4-2.0 in our system using diatomite as starting material along a straight line through the pure zeolite Y regions. However, only amorphous material was obtained as a product for Na$_2$O/SiO$_2$ ratios <0.6 (S0.4 and S0.5 in Table 3.2 and Fig. 3.2), while mixtures consisting of zeolite FAU and P were obtained when the Na$_2$O/SiO$_2$ ratio was 0.6–0.9. By further increasing the Na$_2$O/SiO$_2$ ratio, zeolite P was the only product in samples S1.0, S1.2, and S2.0.

Figure 3.3. SEM of S0.6 at 48 hours

Sample S0.6 obtained after 48 hours of synthesis time showed evident signs of overrun as revealed by SEM (Figure 3.3); well-defined tetragonal crystals attributed to zeolite P appeared to grow on dissolving FAU zeolite crystals. Both zeolites showed comparable SiO$_2$/Al$_2$O$_3$ ratios, namely 4.36 for FAU and 4.30 for P as determined by XRD and EDS, respectively. This agreed with the fact that the XRD pattern of zeolite P was very close to that reported by Hansen et al. for high silica tetragonal NaP with a SiO$_2$/Al$_2$O$_3$ ratio of 6.9 (PDF 40-1464) [51]. Such nucleation and growth of zeolite P on dissolving faujasite has already been observed by scanning and transmission electron microscopy [52, 53]. It is well-known that zeolite P is a more stable phase than zeolite FAU and that the former can nucleate and grow before complete formation of the latter [54]. Therefore, to maximize the yield of the FAU zeolite and to limit the formation of zeolite P, synthesis time was reduced below 48 h for S0.6, S0.7, S0.8, S0.9, S1.2 and S2.0.
Figure 3.4. XRD diffractograms of the solid products obtained after different synthesis times for: (A) S0.6; (B) S0.7; (C) S0.8; (D) S0.9; (E) S1.2; and (F) S2.0.

Figure 3.4(A) for S0.6 shows that zeolite P was found to be absent by XRD as synthesis time was reduced to 30 h. However, the XRD results also indicated the presence of appreciable amounts of amorphous material. Hence, it was not possible to obtain well-crystallized FAU zeolite for composition S0.6. Similar behavior was observed for S0.7 (Figure 3.4(B)), for which 28 h was the optimal time to avoid the presence of zeolite P. FAU
zeolite, free from zeolite P and amorphous material, was obtained when synthesis time was 15 h for S0.8 (Fig. 3.4(C)). Reducing time to 13h, 6h and 6h for syntheses S0.9, S1.2 and S2.0, respectively, prevented the formation of zeolite P and resulted in FAU-type zeolite with high crystallinity as the only product, as shown in Fig. 3.4(D), Fig. 3.4(E) and Fig. 3.4 (F), respectively.

Table 3.3 gives the SiO$_2$/Al$_2$O$_3$ ratio in the FAU crystals determined by X-ray diffraction for the different Na$_2$O/SiO$_2$ ratios in the synthesis mixture and as a function of synthesis time. For each synthesis, the observed values are constant within deviations of ±0.2 which was found to be the precision of the method by reproducing the same synthesis several times, except S0.6. As shown above, after the optimal synthesis time, zeolite P appeared in all cases and the FAU particles started to dissolve. Therefore, the nucleation of zeolite P and subsequent dissolution of FAU-zeolite resulted in a rather constant measured SiO$_2$/Al$_2$O$_3$ ratio in the dissolving FAU crystals; however, S0.6 showed a strong decrease of this parameter along with dissolution of the FAU crystals. This suggests that the core of the FAU crystals is Al-rich in S0.6.

**Table 3.3.** SiO$_2$/Al$_2$O$_3$ composition determined by XRD of the FAU products from optimal synthesis time and further on.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na$_2$O/SiO$_2$</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6h</td>
<td>9h</td>
</tr>
<tr>
<td>S0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>4.8</td>
</tr>
<tr>
<td>S0.7</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.7</td>
</tr>
<tr>
<td>S0.8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S0.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>S1.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>S2.0</td>
<td>2.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>
3.1.1.3. Characteristics of the final product

**Figure 3.5.** Scanning electron micrographs of (A) S2.0-6h; (B) S1.2-6h; (C) S0.9-13h; (D) S0.8-15h; (E) S0.7-28h; (F) S0.6-30h.

SEM images (Figure 3.5) of all samples obtained after optimal synthesis time, showed that all samples contained euhedral particles consisting of more or less intergrown crystals with
octahedral symmetry. Particle size clearly increased as alkalinity was decreased by lowering the Na$_2$O/SiO$_2$ ratio from 2.0 to 0.7 (Fig. 3.5(A)-Fig. 3.5(E)), specifically from 0.5 µm (S2.0-6h) to 2.3 µm (S0.7-28h). The degree of intergrowth also clearly diminished with lowering the Na$_2$O/SiO$_2$ ratio in the same range. The crystals in S2.0-6h were irregular due to strong intergrowth, while increasingly more well-defined crystals with octahedral symmetry formed as the Na$_2$O/SiO$_2$ ratio was progressively decreased. However, particle size was found to decrease and the degree of intergrowth to increase again for S0.6-30h (Fig. 3.5(F)). For the Na$_2$O/SiO$_2$ ratios less than or equal to 0.8, the presence of unreacted materials becomes obvious (Fig. 3.5(D) to Fig. 3.5(F)). Large non-reacted diatomite skeletons were still present in S0.6-30h which clearly indicates that alkalinity was insufficient to digest the raw materials for Na$_2$O/SiO$_2$ ratios below 0.9.

3.1.1.4. Discussion

Table 3.4 shows the yield in terms of silicon ($\eta_{Si}$) and aluminum ($\eta_{Al}$) calculated from gravimetric measurements and ICP-SFMS. Interestingly, both types of yield are fairly constant for all samples after optimal synthesis time. Yield in terms of silicon varies between 0.34 and 0.41 with no clear trend with regard to dependency on the Na$_2$O/SiO$_2$ ratio, while the values expressed on the basis of aluminum oscillates around 1.

The SiO$_2$/Al$_2$O$_3$ ratios of the final products determined by ICP-SFMS ($R_{ICP}$ in Table 3.4) were corrected by assuming 100% yield with respect to aluminum in the following way:

$$R_{ICP}^* = R_{ICP} \times \eta_{Al}$$  \hspace{1cm} (1)

The corrected SiO$_2$/Al$_2$O$_3$ ratios are denoted $R_{ICP}^*$ in Table 3.4. The $R_{ICP}^*/R_{start}$ ratio gives, as expected, the overall yield in solid product with respect to silica determined by ICP-SFMS and gravimetrically, according to equation (2):

$$R_{ICP}^*/R_{start} = \frac{\eta_{SiO_2 final product}}{\eta_{Al_2O_3 final product}} / \frac{\eta_{SiO_2 start}}{\eta_{Al_2O_3 start}} = \frac{\eta_{SiO_2 final product}}{\eta_{SiO_2 start}}$$  \hspace{1cm} (2)

Although the overall yields with respect to silica are rather constant, the amount of zeolite produced depends strongly on alkalinity. This amount can be roughly estimated from the measured microporosity yield and X-ray crystallinity and are reported in comparison with commercial zeolite Y powder (Table 3.4). The microporosity yield values were higher than those for X-ray crystallinity for Na$_2$O/SiO$_2$ ratios >0.7, and part of the unreacted material can
be microporous. Also, the sensitivity of X-ray diffractions is a few per cent for detecting one phase within another [55]. Therefore, the actual yield of FAU zeolite can be expected to lie in-between these two values. High values of the microporosity yield and X-ray crystallinity were obtained for Na₂O/SiO₂ ratios between 0.9 and 2.0 but dropped dramatically as alkalinity was decreased for Na₂O/SiO₂ ratios below 0.9.

Table 3.4. Yield, SiO₂/Al₂O₃ ratios and comparison of the later for all best syntheses.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield in terms of Si (mol%)</th>
<th>Yield in terms of Al (mol%)</th>
<th>Starting SiO₂/Al₂O₃ ratio (RICP)</th>
<th>ICP-SFMS SiO₂/Al₂O₃ ratio (RICP)</th>
<th>ICP-SFMS SiO₂/Al₂O₃ ratio (RICP*)</th>
<th>RxRD RICP*</th>
<th>XRD SiO₂/Al₂O₃ ratio (RXRD)</th>
<th>RxRD RICP*</th>
<th>Microporous yield</th>
<th>X-ray crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0.6</td>
<td>0.41</td>
<td>0.97</td>
<td>11.05</td>
<td>4.7</td>
<td>4.5</td>
<td>0.41</td>
<td>5.3</td>
<td>1.17</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>S0.7</td>
<td>0.35</td>
<td>0.92</td>
<td>11.05</td>
<td>4.3</td>
<td>3.9</td>
<td>0.35</td>
<td>4.7</td>
<td>1.21</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>S0.8</td>
<td>0.37</td>
<td>0.99</td>
<td>11.05</td>
<td>4.2</td>
<td>4.1</td>
<td>0.37</td>
<td>4.1</td>
<td>0.99</td>
<td>0.63</td>
<td>0.48</td>
</tr>
<tr>
<td>S0.9</td>
<td>0.34</td>
<td>0.87</td>
<td>11.05</td>
<td>4.4</td>
<td>3.8</td>
<td>0.34</td>
<td>3.9</td>
<td>1.02</td>
<td>1.03</td>
<td>0.81</td>
</tr>
<tr>
<td>S1.2</td>
<td>0.37</td>
<td>1.13</td>
<td>11.05</td>
<td>3.6</td>
<td>4.1</td>
<td>0.37</td>
<td>3.0</td>
<td>0.73</td>
<td>0.83</td>
<td>0.73</td>
</tr>
<tr>
<td>S2.0</td>
<td>0.38</td>
<td>1.36</td>
<td>11.66</td>
<td>3.3</td>
<td>4.4</td>
<td>0.38</td>
<td>3.4</td>
<td>0.76</td>
<td>0.89</td>
<td>0.69</td>
</tr>
<tr>
<td>zY com</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
<td>5.2</td>
<td>-</td>
<td>5.2</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

By comparing the SiO₂/Al₂O₃ ratio in the zeolite, determined by XRD, with the corrected ICP-SFMS SiO₂/Al₂O₃ ratio in the final product (RXRD/RICP* in Table 3.4), it is clear that the unreacted solid is Al-rich in S0.6-30h and S0.7-28h, while both the unreacted solid and the zeolite have approximately similar SiO₂/Al₂O₃ ratios for S0.8-15h and S0.9-13h. Increasing alkalinity further causes RXRD/RICP* values to drop below 1, which indicates that the unreacted solid must be Si-rich. In fact, RXRD/RICP* can be expressed in terms of moles as follows:

$$\frac{RXRD}{RICP^*} = \frac{\frac{n_{SiO2 \ \text{zeolite}}}{n_{Al2O3 \ \text{zeolite}}} / \frac{n_{SiO2 \ \text{final product}}}{n_{Al2O3 \ \text{final product}}} = \frac{n_{SiO2 \ \text{zeolite}}}{n_{SiO2 \ \text{final product}}} \times \frac{n_{Al2O3 \ \text{final product}}}{n_{Al2O3 \ \text{zeolite}}}}$$

(3)

The last factor in eq. (3) must be larger or equal to 1 if all the aluminum in the final product is located in the zeolite and RXRD/RICP* represents the zeolite yield with respect to silica in the
solid product. The values of $R_{\text{XRD}}/R_{\text{ICP}}$ of 0.73 and 0.76 obtained for S1.2-6h and S2.0-6h, respectively, lie in between the corresponding values of XRD crystallinity and microporous yield. This indicates that most of the aluminum, if not all, is located in the zeolite crystals.

Two conclusions can be drawn from these results: (i) S1.2-6h and S2.0-6h produced FAU crystals with 100% yield regarding to the aluminum initially introduced; (ii) since 6h is enough for obtaining pure FAU zeolite for both compositions, then it is the depletion in aluminum that triggered the formation of zeolite P. In fact, the apparent SiO$_2$/Al$_2$O$_3$ ratio measured by XRD clearly decreased as the FAU crystals started to dissolve and zeolite P began to grow (Table 3.3), indicating that less aluminum was included in the latest stages of growth of the FAU crystals before onset of dissolution. It is known that growth of FAU zeolites ceases as aluminum is depleted, which renders the synthesis of high silica faujasite difficult. This is usually assigned to the fact that aluminate ions are necessary for the formation of sodalite cages, which are part of the FAU structure [56].

The SiO$_2$/Al$_2$O$_3$ ratio in the zeolite ($R_{\text{XRD}}$ in Table 3.4) increased steadily as alkalinity decreased in our system using diatomite as silica source. In fact, it has been shown by different research groups that the SiO$_2$/Al$_2$O$_3$ ratio increases in various zeolites as the excess alkalinity decreases [57, 58]. Fewer nucleation events and decreased supersaturation conditions resulted by slow liberation of silica from diatomite as alkalinity was reduced; this caused an increase in size of the FAU crystals. This fact was also confirmed by preliminary results obtained by gravimetric analysis and ICP-SFMS, which indicates that 11% and 0.5% of all silicon introduced was present in the supernatant after 24 h aging for composition S2.0 and S0.6. In contrast, the supernatant contained approximately 50% of all aluminum introduced for both compositions, which certainly originated from aluminum sulfate.

Interestingly, the synthesis of high silica faujasite usually requires the use of colloidal silica, since FAU crystals with SiO$_2$/Al$_2$O$_3$ ratios larger than 3.9 cannot be obtained in the SiO$_2$-Al$_2$O$_3$-Na$_2$O-H$_2$O system by utilizing sodium silicate [3]. The use of diatomite also allowed SiO$_2$/Al$_2$O$_3$ ratios larger than 3.9 similar to the behavior for colloidal silica proposed by Breck and Flanigen (Figure 3.2). Both silica sources are similar, in that they both have a higher degree of polymerization of silica than sodium silicates. However, diatomite was too bulky to be completely consumed under the investigated synthesis conditions.
Breck and Flanigen’s [3] and Rüscher et al. [39] argued that both domains of zeolite X and Y exist above SiO₂/Al₂O₃ ratio of 3 and that pure zeolite Y can only be claimed if this is greater than or equal to 5.4. In light of these definitions, all final products obtained in this work is zeolite Y. However, syntheses S2.0-6h and S1.2-6h produced FAU crystals with SiO₂/Al₂O₃ ratios close to 3 (see Table 3.3), which therefore can be said to mainly consist of zeolite X with very few zeolite Y domains. Lowering the Na₂O/SiO₂ ratio until S0.6-30h produced crystals with an average SiO₂/Al₂O₃ ratio of 5.3 (Table 3.4) and low crystallinity. However, both Breck and Flanigen’s and Rüscher’s studies showed that crystals with a SiO₂/Al₂O₃ ratio higher than 3.8 could present hydrothermal stability only inferior by approximately 10% to that obtained for high-silica zeolite Y after steaming at 410°C for 3 h or 500°C for 5 h, respectively. Therefore, the product of synthesis S0.9-13h, which showed a SiO₂/Al₂O₃ ratio of 3.9 and high crystallinity, may be a stable and inexpensive alternative for FCC catalysts.

3.1.2. ZSM-5 (Paper III)

3.1.2.1. Characteristics of the starting materials

X-ray diffractograms of the raw diatomite and its dealuminated counterpart did not differ from the diffractograms shown in Figure 3.1 when changing the acid source, i.e. replacing H₂SO₄ for HCl. Hence, refer to Figure 3.1 for mineralogical characterization. After acid treatment and subsequent washing, the amorphous material remained and NaCl was removed, but the other minor constituents were still present (muscovite, albite and quartz).

Table 3.5. Compositions (in molar %) of kaolin, diatomite, leached metakaolin, leached diatomite and ZSM-5 products by ICP-SFMS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Main Components (mol %)</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Diatomite</td>
<td>78.8</td>
<td>5.22</td>
</tr>
<tr>
<td>Leached Diatomite</td>
<td>96.4</td>
<td>2.17</td>
</tr>
<tr>
<td>ZSM-5 (D)</td>
<td>96.0</td>
<td>2.40</td>
</tr>
</tbody>
</table>
The chemical compositions of the raw and leached materials measured by ICP-SFMS are given in Table 3.5. Diatomite had a SiO$_2$/Al$_2$O$_3$ ratio of 15; this ratio was increased by acid leaching to 44. Acid leaching also reduced significantly the concentration of impurities.

![Figure 3.6 SEM images of: a) diatomite and (b) leached diatomite.](image)

Figure 3.6 Shows the morphology of the raw and leached materials revealed by SEM. Raw diatomite (Fig. 3.6(a)) exhibits large particles with typical shapes of diatomaceous biogenic sediments. Some diatomite particles were partially broken in smaller pieces by the mechanical action of stirring during the acid treatment but their characteristic shapes could still be distinguished (Fig. 3.6(b)). Leaching of diatomite only caused a slight increase in specific surface area (from 38 to 55 m$^2$/g, see Table 3.6).

Table 3.6. Surface area and pore volumes derived from nitrogen adsorption data for the raw, leached material, final product and standard sample.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m$^2$/g)</th>
<th>Total Pore Volume (cm$^3$/g)</th>
<th>Micropore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>38</td>
<td>0.093</td>
<td>0.003</td>
</tr>
<tr>
<td>Leached Diatomite</td>
<td>55</td>
<td>0.11</td>
<td>0.006</td>
</tr>
<tr>
<td>ZSM-5 (D)</td>
<td>298</td>
<td>0.15</td>
<td>0.098</td>
</tr>
<tr>
<td>ZSM-5 standard</td>
<td>310</td>
<td>0.15</td>
<td>0.12</td>
</tr>
</tbody>
</table>
3.1.2.2. Characteristics of the crystalline products

For leached diatomite, the best crystallinity was obtained after 12 hours of synthesis time. The diffractogram of the final reaction product obtained after 12 hours is presented in Figure 3.7(a), where the main characteristic peaks correspond to the MFI structure (2θ = 7.9; 8.7; 23.0 etc.) in good agreement with the reference pattern PDF-042-0024. The intensities of the main peak of quartz was similar and of the same order of magnitude as in the leached material. Consequently, the quartz content originated from the raw material. However, the final zeolite product obtained from acid treated diatomite contained traces of mordenite, approximately 5% when compared with the intensity of the main peak of ZSM-5. The composition of the final product after 12 hours of synthesis was determined by ICP-SFMS analysis and the results are presented in Table 3.5. The average SiO₂/Al₂O₃ ratio was 40 for the reaction product obtained from acid treated diatomite. Based on these data, it was concluded that the reaction product could be considered as quite pure ZSM-5 with traces of mordenite (formed during synthesis) as well as quartz remaining from the raw material.

![Figure 3.7.](image)

The SEM image in Figure 3.7(b) shows the morphology of the reaction products obtained from acid treated diatomite. The ZSM-5 crystals obtained from leached diatomite were rounded with an average diameter around 7-8 µm and an aspect ratio close to 1. This sample also contained smaller particles and particularly small slabs as those encircled in Fig. 3.7(b), which were attributed to mordenite.
3.1.2.3. Discussion

As shown above, the combination of both sodium hydroxide and \( n \)-butylamine together with leached diatomite was efficient to produce micron-sized ZSM-5 crystals. The maximum crystallinity for samples prepared from diatomite was 93% by referring to a pure ZSM-5 zeolite. By a normalization of the BET specific surface area with respect to the ZSM-5 standard sample, it was found that the value for crystallinity calculated from the BET (96%) is higher than that obtained by XRD (93%). This can be attributed to the presence of mordenite as a by-product in addition to non-microporous materials.

It was not possible to prevent the formation of mordenite by further optimization of the synthesis parameters. Instead, formation of mordenite occurred randomly, probably due to the variability of the diatomaceous earth raw material. Calcium was found to be concentrated in the mordenite crystals as revealed by the comparison of the EDS spectra between uncalcined ZSM-5 (Fig. 3.8(a)) and mordenite crystals (Fig. 3.8(b)). Therefore, the high calcium content in diatomite probably favored the formation of mordenite. The presence of \( n \)-butylamine as templating agent in the ZSM-5 crystals was also confirmed by EDS, as shown in Fig. 3.8(a) with the characteristic peak of nitrogen and carbon, while the peak corresponding to sodium was quite weak.

![Figure 3.8. EDS spectra of: (a) a ZSM-5 crystal and (b) a mordenite crystal in the final product obtained from leached diatomaceous earth after 12 h synthesis.](image)

The BET specific surface area obtained in this work for the sample prepared from leached diatomaceous earth (298 m\(^2\)/g) was comparable with that obtained in the study by Sang et al.
[59] (294 m²/g), who employed water glass and aluminum sulfate as Si and Al sources, respectively. Therefore, Bolivian diatomaceous earth appears as a competitive source of inexpensive raw materials for the synthesis of ZSM-5 crystals. In addition to the higher crystallinity and BET specific surface area achieved in this work, diatomaceous earth does not require heat treatment at high temperature for metakaolinization commonly used in similar synthesis with kaolin.

3.2. Syntheses from Bolivian montmorillonite and commercial kaolin (paper II)

3.2.1. Synthesis of zeolite A by alkali fusion

The diffractogram of the raw RMA clay (Figure 3.9A) showed the characteristic peaks of montmorillonite at 2θ = 5.9, 19.8 and 35° as compared with PDF patterns, but also the occurrence of quartz in low content. Raw kaolin (KFA in Figure 3.9C) contained mostly kaolinite as evidenced by reflections at 2θ = 12.33; 19.80; 20.40; 21.40; 24.81 and 35.11, but also traces of quartz and muscovite. The elemental compositions of the RMA and KFA clays obtained by ICP-SFMS are given in Table 3.7. Besides alumina, calcium and magnesium were present in appreciable amounts in the Bolivian montmorillonite in comparison to kaolin. However, both clays contained similar amounts of iron, i.e. 0.79-0.82 wt. % Fe₂O₃.

Table 3.7. Main components of the raw materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Main components (wt. %)</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>RMA</td>
<td>63.75</td>
<td>21.95</td>
</tr>
<tr>
<td>KFA</td>
<td>54.43</td>
<td>42.87</td>
</tr>
</tbody>
</table>

Montmorillonite and quartz (as well as kaolin) suffered a structural reorganization during alkali fusion at 873 K. Fused RMA and fused KFA resulted in formation of different sodium aluminosilicates, i.e. Na₂SiO₃, Na₂Al₂O₄, Na₄Al₅Si₈O₂₆, etc. as shown in Fig. 3.9B and Fig. 3D. All compounds formed after alkali fusion of the starting clays could be readily dissolved in water and serve as reactants for zeolite synthesis in combination with sodium aluminate and sodium hydroxide.
Figure 3.9. XRD diffractograms of: (A) RMA; (B) fused RMA; (C) KFA and (D) fused KFA.

Figure 3.10 shows the XRD diffractograms of the final products after hydrothermal treatment at 373 K after different synthesis times. When a molar SiO$_2$/Al$_2$O$_3$ ratio of two was used, 3 and 4 hours of hydrothermal treatment were required to obtain zeolite A as a unique product with high crystallinity for the RMA and KFA clays, respectively (RMA(2.0)-3h and KFA(2.0)-4h in Figure 3.10). Appreciable amounts of amorphous material were present in samples if shorter synthesis times were used (RMA(2.0)-2h and KFA(2.0)-3h in Figure 3.10). Table 3.8 shows the overall SiO$_2$/Al$_2$O$_3$ ratios of the final products determined by EDS. RMA(2.0)-3h was found to contain an excess of silica with a SiO$_2$/Al$_2$O$_3$ ratio of 2.36 compared to the ideal ratio of 2.0. Therefore, the molar SiO$_2$/Al$_2$O$_3$ ratio in the RMA synthesis mixture was varied in the range 1.15-2.0. Decreasing this ratio from 2 to 1.8 resulted in a slight decrease of the SiO$_2$/Al$_2$O$_3$ ratio in the product to 2.22, see RMA(1.8)-3h in Table 3.8 and Figure 3.10. However, by further lowering this ratio by increasing the amount of aluminum in the synthesis mixture resulted in a steady decrease in crystal size, while the SiO$_2$/Al$_2$O$_3$ ratio in the product was almost constant. The RMA sample prepared with a molar SiO$_2$/Al$_2$O$_3$ ratio of 1.8 was also mainly amorphous for synthesis times shorter than 3 h, e.g. RMA(1.8)-2h in Figure 3.10.
Figure 3.10. XRD diffractograms of the following samples: RMA(2.0)-2h; RMA(2.0)-3h; RMA(1.8)-2h; RMA(1.8)-3h; KFA(2.0)-3h and KFA(2.0)-4.

Table 3.8. Compositional ratios in the final products determined by EDS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion exchange</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>Na/Al</th>
<th>2Ca/Al</th>
<th>2Mg/Al</th>
<th>(Na+2Ca)/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>commercial</td>
<td>-</td>
<td>2.08</td>
<td>0.99</td>
<td>n. d.</td>
<td>n. d.</td>
<td>0.99</td>
</tr>
<tr>
<td>RMA(2.0)-3h</td>
<td>-</td>
<td>2.36</td>
<td>0.87</td>
<td>0.11</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>-</td>
<td>2.22</td>
<td>0.90</td>
<td>0.12</td>
<td>0.19</td>
<td>1.02</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>Na</td>
<td>2.28</td>
<td>0.93</td>
<td>0.03</td>
<td>0.18</td>
<td>0.96</td>
</tr>
<tr>
<td>KFA(2.0)-4h</td>
<td>-</td>
<td>2.22</td>
<td>0.97</td>
<td>0.01</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>-</td>
<td>2.16</td>
<td>0.99</td>
<td>n. d.</td>
<td>0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>Na</td>
<td>2.28</td>
<td>0.98</td>
<td>0.01</td>
<td>0.16</td>
<td>0.99</td>
</tr>
</tbody>
</table>

n. d. (non-detected)
3.2.2. Size and morphology of the particles

Figure 3.11 shows SEM micrographs of RMA(1.8)-3h, KFA(2.0)-4h and the commercial powder.

**Figure 3.11.** SEM micrographs of: (A)-(B) RMA-3; (C)-(D) KFA-4; (E)-(F) commercial zeolite A.
As shown in Fig. 3.11 (A), RMA(1.8)-3h consisted of cubic crystals ranging between 0.5-1.5 µm in length. Part of the crystals exhibited intergrowth, which is usually explained by a high concentration of nuclei [60]. Fig. 3.11(B) reveals that the larger crystals possessed chamfered edges, which is suitable for detergent grade zeolites. The zeolite crystals of the KFA(2.0)-4 sample showed similar characteristics, except for a slight increase in length to approximately 1-2 µm (Fig. 3.11(C) and Fig.3.11(D)). Comparatively, the crystals in the commercial powder were found to measure between 1 and 7 µm (Fig. 3.11(E)) and to be relatively intergrown (Fig. 3.11(F)).

### 3.2.3. Brightness measurements

Table 3.9 shows the results of the brightness and yellowness measurements which were performed on RMA(1.8)-3h, KFA(2.0)-4h and the commercial powder. With 94.5% brightness and 3.0% yellowness, the sample obtained from Rio Mulatos clay after optimal synthesis time (RMA(1.8)-3h) showed excellent optical properties. These values were superior to those of the commercial powder, i.e. 92.6% brightness and 3.8% yellowness. In comparison, the sample produced from commercial kaolin was found to exhibit a slight orange color to the naked eye. This was confirmed by the poor brightness and relatively high yellowness values obtained for KFA(2.0)-4h in Table 3.9, i.e. 76.4% and 14.4%, respectively. These values are typical of zeolite A powder synthesized from metakaolin. Therefore, the method to activate kaolin did not seem to influence the final color of the zeolite A powder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness</th>
<th>Yellowness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial powder</td>
<td>92.6</td>
<td>3.8</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>94.5</td>
<td>3.04</td>
</tr>
<tr>
<td>KFA(2.0)-4h</td>
<td>76.4</td>
<td>14.4</td>
</tr>
<tr>
<td>KFA(2.0)Ca-4h</td>
<td>73.7</td>
<td>11.5</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>82.1</td>
<td>5.4</td>
</tr>
<tr>
<td>KFA(2.0)MgCa-4h</td>
<td>85.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>
3.2.4. Cation Exchange Capacity

As shown in Table 3.8, the commercial zeolite A and KFA(2.0)-4h samples were completely in sodium form, as evidenced by the Na/Al ratios which were estimated to be 0.99 and 0.97, respectively. However, the as synthesized samples obtained by alkali fusion of Rio Mulatos clay were not completely in sodium form but also contained calcium ions that occupied approximately 11-12% of the sites. With regard to cation exchange capacity (CEC), 84% of the exchangeable sites of zeolite A can be compensated by Ca$^{2+}$ cations at 294 K, which represents 592 meq Ca$^{2+}$/100g anhydrous solid. Considering the final SiO$_2$/Al$_2$O$_3$ and 2Ca/Al ratios measured on the RMA(2.0)-3h and RMA(1.8)-3h samples by EDS, maximum CEC values of 480-487 meq Ca$^{2+}$/100g anhydrous solid could be anticipated for these samples. As a matter of fact, loss-on-ignition and ICP-SFMS measurements on the calcium ion exchanged RMA(2.0)-3h sample yielded a value of 487 meq Ca$^{2+}$/100g anhydrous solid. The RMA(1.8)-3h sample was ion exchanged with sodium nitrate to verify that the calcium ions were exchangeable. As shown in Table 3.8, the 2Ca/Al ratio was reduced from 0.12 to 0.03, which showed that this was the case.

3.2.5. Discussion

Usually, the poor brightness and yellowness of zeolite A powders synthesized from kaolin are attributed to iron precipitating into colored impurities (e.g. iron(III) hydroxide) during the aging step and the crystallization process [61]. The iron content was found to be 0.44 and 0.54 wt. % by ICP-SFMS in the RMA(1.8)-3h and KFA(2.0)-4h samples, respectively. Albeit these amounts were in the same order of magnitude and both samples were synthesized by the same method, the corresponding final zeolite products showed very different optical properties in terms of brightness and yellowness.

Referring to Table 3.7, the major compositional difference between the two raw materials investigated in this work was the high content in calcium and magnesium in Rio Mulatos clay. These elements were still present in appreciable amounts in the final products as shown by the EDS results in Table 3.8. Therefore, the difference in optical properties was attributed to a positive effect of one of these (or both) elements. In order to test this hypothesis, amounts of calcium and magnesium similar to those present in RMA clay were added to the synthesis mixture based on KFA clay before alkali fusion using nitrates. Three new products were obtained and denoted KFA(2.0)Ca-4h, KFA(2.0)Mg-4h and KFA(2.0)MgCa-4h depending on
whether only calcium or magnesium or both elements were added, respectively. All final products consisted mostly of zeolite A with minor contents of sodalite (~5%). The results in Table 3.9 showed that the addition of solely calcium slightly improved yellowness. Interestingly, addition of magnesium to kaolin before alkali fusion remarkably enhanced the optical properties of the final powder, independently of whether calcium was added or not. The corresponding brightness and yellowness values were higher than those obtained by Chandrasekhar [24] who employed a complex combination of chemical treatment to reduce the amount of Fe₂O₃ in the final zeolite product to 0.04 wt. %.

The results in Table 3.8 indicated that, in contrast to calcium, magnesium was not ion-exchanged by sodium when exposed to a solution of sodium nitrate, which was consistent with the fact that solvated magnesium ions can barely diffuse into zeolite A. In addition, the fact that all values of the (Na⁺2Ca)/Al ratio were close to 1 strongly suggested that magnesium was not located inside zeolite A. As a matter of fact, Mg could not be detected by local EDS inside zeolite A crystals. This is illustrated by the EDS spectrum of Fig. 3.12(B), which was obtained by point analysis in a zeolite A crystal, i.e. the encircled region in Fig. 3.12(A). Instead, Mg and Fe were found to be concentrated in the extraneous material consisting of platelets and finely divided matter as revealed in the region delimited by the rectangle in Fig. 3.12(A) and the corresponding EDS spectrum in Fig. 3.12(C). Consequently, our data strongly suggest that magnesium exerts a masking effect on iron that becomes incorporated inside aluminosilica compounds in which it is probably substituted for magnesium in the divalent state, thereby limiting typical coloration due to Fe(III). This simple method appears as a promising alternative to complex and costly techniques developed in order to reduce the iron content in natural raw materials.
Figure 3.12. (A) SEM micrograph showing the extraneous matter in RMA(1.8)-3h; EDS analysis of: (B) extraneous matter (dotted square in A) and (C) a zeolite A crystal (dotted circle in A).

4. CONCLUSIONS

In this study, it was shown that Bolivian raw materials could be used as aluminosilica sources for the synthesis of zeolite Y, ZSM-5 and zeolite A with high yield and crystallinity. The main findings regarding each zeolite can be summarized as follows:

Preparation of zeolite Y from diatomite

- After optimization of synthesis time, zeolite Y with low SiO$_2$/Al$_2$O$_3$ ratio (3.0-3.4), 100% yield in terms of aluminum and low amount of extraneous material was
obtained at high alkalinity (Na₂O/SiO₂ = 1.2-2.0). Decreasing alkalinity resulted in an increase of the SiO₂/Al₂O₃ ratio in zeolite Y.

- High zeolite yield could only be achieved down to a Na₂O/SiO₂ ratio of 0.9, which produced zeolite Y with a SiO₂/Al₂O₃ ratio of 3.9. Lower Na₂O/SiO₂ ratios resulted in incomplete dissolution of diatomite and poor zeolite yield.

- It was possible to synthesize almost pure zeolite Y with a SiO₂/Al₂O₃ ratio of 5.3 in low yield at a Na₂O/SiO₂ ratio of 0.6. In this aspect, diatomite behaved closely as colloidal silica in traditional syntheses, both silica sources having in common a high degree of polymerization.

- Finally, overrun of all investigated compositions resulted in the formation of zeolite P nucleating and growing onto dissolving zeolite Y crystals, which was shown to be triggered when aluminum was completely depleted at high alkalinity.

**Preparation of ZSM-5 from diatomite**

- Dealumination of Bolivian diatomite by acid leaching made it possible to reach an appropriate SiO₂/Al₂O₃ ratio of approximately 40 for ZSM-5 synthesis and to reduce the amount of iron and other impurities.

- Our results clearly showed for the first time that well-crystallized ZSM-5 with a SiO₂/Al₂O₃ ratio of 40 could be directly prepared from the low-cost raw materials leached diatomite, sodium hydroxide and n-butyl amine under appropriate synthesis conditions.

**Preparation of zeolite A from montmorillonite and commercial kaolin**

- Zeolite A crystals were successfully synthesized from Bolivian montmorillonite type clay and commercial kaolinite using the alkali fusion method. The crystals had cubic habit with a length ranging between 0.5 and 2 µm and intergrown.

- Although Bolivian montmorillonite and commercial kaolinite contained similar concentration of iron, they radically differed in terms of optical properties. This was attributed to the magnesium present in the Bolivian raw material, which probably forced iron inside colorless extraneous magnesium aluminosilica compounds.

- The masking effect was verified by addition of magnesium to kaolinite. This simple process appears very promising to prepare zeolite A with excellent optical properties from inexpensive natural raw materials.
5. FUTURE WORK

This work has shown the feasibility of preparing valuable zeolites from non-costly Bolivian raw materials. However, there are still many challenges remaining to achieve the original goals of this project. Therefore, it would be necessary to:

- test the catalytic and adsorption properties of the zeolites synthesized by the different procedures in order to assess their performances in the targeted applications.
- tailor the synthesis procedure of zeolite A in order to achieve a SiO$_2$/Al$_2$O$_3$ ratio closer to 1.
- investigate the feasibility of reusing the aluminum-rich solutions produced during leaching of diatomite for the synthesis of zeolite A instead of commercial sodium aluminate.
- investigate the technico-economical possibility of producing these zeolites on an industrial scale in order to contribute to the development of the poor regions in Bolivia.

The work on zeolite Y highlighted how the synthesis of faujasite zeolites is still not clearly understood. Studying some of the different compositions investigated in this study as a function of synthesis time might help to clarify which parameters primarily dominate the growth mechanisms of this type of zeolitic material.
6. REFERENCES


Paper I

Synthesis of zeolite Y from diatomite as silica source

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Synthesis of zeolite Y from diatomite as silica source

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Abstract

Bolivian diatomite was successfully used as a silica source for the synthesis of zeolite Y. Prior to synthesis, the diatomite was leached with sulfuric acid to remove impurities and aluminum sulfate was used as an aluminum source. The raw materials were reacted hydrothermally at 373 K in water with sodium hydroxide and different Na₂O/SiO₂ ratios were investigated. The final products were characterized by scanning electron microscopy, X-ray diffraction, gas adsorption and inductively coupled plasma-atomic emission spectroscopy. After optimization of synthesis time, zeolite Y with low SiO₂/Al₂O₃ ratio (3.0-3.4), 100% yield in terms of aluminum and low amount of extraneous material was obtained at high alkalinity (Na₂O/SiO₂ = 1.2-2.0). Decreasing alkalinity resulted in an increase of the SiO₂/Al₂O₃ ratio in zeolite Y. However, high zeolite yield could only be achieved down to a Na₂O/SiO₂ ratio of 0.9, which produced zeolite Y with a SiO₂/Al₂O₃ ratio of 3.9. Lower Na₂O/SiO₂ ratios resulted in incomplete dissolution of diatomite and poor zeolite yield. Nevertheless, it was possible to synthesize almost pure zeolite Y with a SiO₂/Al₂O₃ ratio of 5.3 at a Na₂O/SiO₂ ratio of 0.6, albeit with a low yield. In this respect, diatomite behaved similarly to colloidal silica in traditional syntheses, with both sources of silica having a high degree of polymerization. Finally, overrun of all investigated compositions resulted in nucleation and growth of zeolite P onto zeolite Y crystals, which was shown to be triggered when aluminum was completely depleted at high alkalinity.
Keywords:
Faujasite, zeolite P, diatomite

1. Introduction

Zeolites are crystalline aluminosilicate molecular sieves with unique properties. These compounds are comprised of a three-dimensional network of silicon and aluminum oxide tetrahedrons (SiO$_4$ and AlO$_4$-) linked by shared oxygen atoms and containing charge-compensating cations. The resulting structures form porous frameworks with micropores in the range of ~2 to 13 Å [1], which confer them molecular sieving properties. Zeolites also possess very high surface areas due to this microporosity and exhibit variable acidic properties depending on composition. Because of these special properties, they can be used in a wide range of applications such as ion exchange, adsorption, catalysis and membrane separation [2].

Two zeolites of particular interest are zeolite X and zeolite Y. These are faujasite type zeolites (FAU), defined by a SiO$_2$/Al$_2$O$_3$ ratio between 2-3 for zeolite X and greater than 3 for zeolite Y [3]. The basic structural units for this type of zeolite are sodalite cages which form supercages able to accommodate spheres up to 1.2 nm in diameter. The openings to these large cavities are 12-membered oxygen rings with a free diameter of 7.4 Å [4]. Zeolite X can be employed as an adsorbent for CO$_2$ capture [5], but it is mostly used in the detergent industry to compliment or substitute zeolite A due to its high capacity for the removal of Mg$^{2+}$ ions in hard water [6]. Zeolite Y is the most widely employed zeolite catalyst due to its use in fluid catalytic cracking (FCC) for conversion of heavy petroleum molecules into gasoline-range hydrocarbons because of its high size selectivity, high concentration of active acid sites, and thermal stability [7-9].

Traditional methods for synthesizing FAU-type zeolites typically involve chemical grade reagents as starting materials and crystallization from a gel or clear solution under hydrothermal conditions. Typical synthesis mixtures are usually composed of sodium silicates, sodium aluminate, aluminum salts or colloidal silica in a strong alkaline media. Other processes also include seeding to obtain the desired zeolite [10]. However, synthesis of zeolites from low cost raw materials has also been
investigated, since chemical grade reagents are expensive. Until now, the use of materials such as kaolin [11], high silica bauxite [12], halloysite [13], interstratified illite-smectite [14], montmorillonite [15], bentonite [16], and incinerated ash [17] has been reported. Of these raw materials, kaolin has been the most extensively studied, since its composition in terms of SiO₂/Al₂O₃ ratio corresponds to that of zeolite A. Consequently, an additional source of silica is required in order to increase the SiO₂/Al₂O₃ ratio for the synthesis of FAU-type zeolites from kaolin.

Diatomite, a type of siliceous biologic sedimentary rock, is an attractive raw material with high silica content. It contains mainly amorphous silicon oxide derived from biogenic siliceous sediments (unicellular algae skeletons, frustules) and is available in bulk quantities at low cost [18]. Being amorphous and silica rich, diatomite does not require any additional heat treatment or silica source for use in the synthesis of FAU-type zeolites, both of which represent additional costs [19]. However, the occurrence of CaCO₃ and Fe as impurities is quite common in diatomite type materials [20] and adequate treatments must be employed for purification [21]. Moreover, potassium, which is known to promote the formation of zeolite P [22], is also common in this kind of raw material meaning that a reduction in potassium content is required.

A number of groups have reported the use of diatomite as raw material for zeolite synthesis [23-26]. However, to the best of our knowledge, there are very few reports about the synthesis of FAU-type zeolites using diatomites as the silicate source. This is probably due to the difficulty of synthesizing a highly crystalline product consisting of FAU-type zeolites without contamination from zeolite P, which is often grown as a main secondary product [27]. Li et al. reported the use of diatomite to form pure zeolite Y [28]. However, a technique based on fusion and seeding was used to obtain pure zeolite Y and prevent the formation of zeolite P. The synthesis of zeolite Y with good properties, for use in FCC, was also reported Li et al. using a combination of specially treated kaolin and diatomite with a special seeding technique without the involvement of external Al- or Si-containing chemicals [29].

In the present work, we report on the synthesis of FAU-type zeolite with different SiO₂/Al₂O₃ ratios from diatomite with high crystallinity and yield. The effect of varying the Na₂O/SiO₂ ratio and
synthesis time at constant SiO$_2$/Al$_2$O$_3$ and H$_2$O/Na$_2$O ratios in the SiO$_2$-Al$_2$O$_3$-Na$_2$O-H$_2$O system is discussed. No energy consuming fusion and no (costly) seeds are needed in the method presented here.

2. EXPERIMENTAL

2.1 Materials

Diatomite originating from the Murmuntani zone, near Llica in the Potosi region of Bolivia, was used as aluminosilicate source. Aluminum sulfate octadecahydrate in powder form (Al$_2$(SO$_4$)$_3$ * 18H$_2$O, Riedel-de Haën, p.a., > 99%) was employed to adjust the SiO$_2$/Al$_2$O$_3$ ratio to that of typical syntheses of zeolite Y. The alkalinity of the synthesis mixture was regulated with sodium hydroxide (NaOH, Sigma Aldrich, p.a., ≥ 98%). Silicon (Merck, p.a., >99) was used to calibrate the peak position during XRD experiments. The unit cell dimension was determined from the data and used to estimate the SiO$_2$/Al$_2$O$_3$ ratio in the crystals. A commercial powder of zeolite Y (Akzo Nobel, CBV100L-T) was used as reference sample for comparison of the results obtained by nitrogen gas adsorption and X-ray diffraction.

2.2 Synthesis procedure

The raw diatomite (DA) was crushed and treated with 6M H$_2$SO$_4$ at 373 K for 24 hours in an autoclave under hydrothermal conditions, rinsed with distilled water until pH 7 and dried overnight. Acid treated diatomite (aDA) as well as a suitable amount of Al$_2$(SO$_4$)$_3$, to adjust the SiO$_2$/Al$_2$O$_3$ molar ratio, was added to NaOH solutions of different concentrations whilst stirring. The molar ratios of the synthesis mixtures were: Na$_2$O/SiO$_2$ = 0.4 – 2.0; SiO$_2$/Al$_2$O$_3$ = 11; H$_2$O/Na$_2$O = 40. These solutions were aged with stirring at room temperature in glass beakers for 24 hours. At the end of the aging period, the reaction mixture was transferred to Teflon-lined autoclaves. The autoclaves were placed in an oven kept at 373 K for different periods of time. At the end of the hydrothermal treatment, the autoclaves were quenched in cold water. The solid product was separated from the reaction mixture by suction filtering using filter paper grade 00H. The solid product was repeatedly filtered and dispersed in distilled water until the pH of the filtrate liquid was less than 9. The final solid product was dried in an
oven at 373 K overnight and weighed in order to estimate the yield.

2.3 Characterization

To determine the chemical composition of the diatomite, acid treated diatomite and final products, inductively coupled plasma – inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) was carried out: 0.1 g sample was digested with 0.375 g of LiBO₂ and dissolved in HNO₃. Loss on ignition (LOI) was determined by heating the sample to 1273K. The mineralogical composition of the raw materials and final products were determined by X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer, equipped with a PixCel3D detector and a graphite monochromator. CuKα1 radiation with λ = 1.540598 Å at 45 kV and 40 mA was used and 2θ was varied in the range 5-50° at a scanning speed of 0.026°/s. The peaks observed in the diffractograms were compared with the powder diffraction files (PDF) database. The SiO₂/Al₂O₃ ratio of the FAU zeolites was calculated by determining the lattice parameter from the (555) reflection of faujasite and using the empirical relationship proposed by Rüscher et al. [30]. Crystallinity was determined by calculating the area under the peaks in the 2θ =31.0-32.5° region after background removal and comparing it to that obtained for a commercial zeolite Y powder. The morphology of the raw materials, intermediate products and final products were studied by extreme high resolution-scanning electron microscopy using an XHR-SEM Magellan 400 instrument supplied by the FEI Company. The samples were investigated using a low accelerating voltage and no conductive coating was used. Nitrogen adsorption at 77 K was recorded using a Micromeritics ASAP 2010 instrument. Specific surface area was determined using the Brunauer–Emmett–Teller (BET) method. The micropore volume of the final products was determined by the t-plot method using the formula:

\[
t = \left[ \frac{13.9900}{0.0340 - \log \left( \frac{P}{P_0} \right)} \right] 0.5000
\] (1)

Yield was also determined from the micropore volume of the samples by comparing their micropore volumes with the value of the commercial powder of zeolite Y.
3. Results

3.1. Starting materials

The XRD diffractogram of the raw diatomite (Figure 1) indicates the presence of halite (NaCl), calcite (CaCO₃), quartz and amorphous silica as main components, as well as muscovite and albite as secondary components, which is typical of diatomites of this type [31]. The presence of halite (and potassium chloride) is expected, since the raw material originates from Llica, a region near the Uyuni salt lake. The composition of the original diatomite obtained by ICP-SFMS is given in Table 1. The main elements in raw diatomite (DA) are silicon and aluminum, but Fe, Na, Ca, K and Mg are also present as impurities.

![Figure 1](image_url). XRD diffractograms of (A) raw diatomite DA and (B) acid treated diatomite aDA.
Table 1. Chemical composition of raw diatomite (DA) and the acid treated diatomite (aDA) determined by ICP-SFMS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (%)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>DA</td>
<td>61.58</td>
<td>6.94</td>
</tr>
<tr>
<td>aDA</td>
<td>94.45</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Comparison between the XRD (Figure 1) and ICP-SFMS results (Table 1) of the original material and the acid treated diatomite (aDA) shows that sodium (and potassium) chloride was removed by rinsing and that the major impurity content was considerably reduced by the leaching treatment. In fact, after leaching only quartz, minor components (muscovite and albite) and calcium were still present in appreciable amounts, but the latter no longer appears to be present in a crystalline form. However, the SiO₂/Al₂O₃ ratio was increased from 15 to 46. Therefore, aluminum sulfate, an inexpensive salt, was added to the synthesis mixture in order to adjust the SiO₂/Al₂O₃ ratio to suitable levels.

3.2. Synthesis optimization

In order to optimize the synthesis of zeolite Y, different compositions were investigated at fixed aging and synthesis temperatures and times, see Table 2.
### Table 2. Composition and synthesis conditions for sample S0.4 to S2.0.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar composition</th>
<th>Ageing</th>
<th>Heating</th>
<th>Main product (secondary product within brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO2/Al2O3</td>
<td>Na2O/SiO2</td>
<td>H2O/Na2O</td>
<td>Time (h)</td>
</tr>
<tr>
<td>S2.0</td>
<td>11.6</td>
<td>2.0</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S1.2</td>
<td>11.1</td>
<td>1.2</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.9</td>
<td>11.1</td>
<td>0.9</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.8</td>
<td>11.1</td>
<td>0.8</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.7</td>
<td>11.1</td>
<td>0.7</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.6</td>
<td>11.6</td>
<td>0.6</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.5</td>
<td>11.6</td>
<td>0.5</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>S0.4</td>
<td>11.5</td>
<td>0.4</td>
<td>40</td>
<td>24</td>
</tr>
</tbody>
</table>

* FAU = zeolite Y, P = zeolite P

**Figure 2.** SiO2 – Al2O3 – Na2O phase diagram showing the distribution of the samples synthesized at different Na2O/ SiO2 ratios (see ref. 3 for more information related to the two highlighted regions).
As shown in the SiO$_2$ – Al$_2$O$_3$ – Na$_2$O phase diagram in Figure 2, the Na$_2$O/SiO$_2$ ratio in the present work was varied in the range 0.4-2.0 in order to move along a straight line through the pure zeolite Y regions reported by Breck and Flanigen [3]. In fact, two different compositional regions were identified by these authors depending on whether sodium silicate or colloidal silica was used as silica source. In our system, using diatomite as starting material, only amorphous material was obtained as a product for Na$_2$O/SiO$_2$ ratios <0.6 (S0.4 and S0.5 in Table 2 and Fig. 2), while mixtures consisting of zeolite FAU and P were obtained when the Na$_2$O/SiO$_2$ ratio was 0.6 – 0.9. By further increasing the Na$_2$O/SiO$_2$ ratio, zeolite P was the only product in samples S1.0, S1.2 and S2.0.

![Figure 3. SEM of S0.6 at 48 hours.](image)

As shown in Figure 3, scanning electron microscopy revealed evident signs of overrun (i.e. zeolite P) in sample S0.6 after 48 hours of synthesis time. Well-defined tetragonal crystals attributed to zeolite P appear to grow on dissolving FAU zeolite crystals. Both zeolites showed comparable SiO$_2$/Al$_2$O$_3$ ratios, namely 4.36 for FAU and 4.30 for P as determined by XRD and EDS, respectively. This fits with the fact that the XRD pattern of zeolite P is very close to that reported by Hansen et al. for high silica tetragonal NaP with a SiO$_2$/Al$_2$O$_3$ ratio of 6.9 (PDF 40-1464) [32]. Such nucleation and growth of zeolite P on dissolving faujasite has already been observed by scanning and transmission electron microscopy [33, 34]. It is well-known that zeolite P is a more stable phase than zeolite FAU and that the former can nucleate before complete formation of the latter [35]. Therefore, to maximize the yield.
of the FAU zeolite and to limit the formation of zeolite P, synthesis time was reduced below 48 h for S0.6, S0.7, S0.8, S0.9, S1.2 and S2.0.

Figure 4. XRD diffractograms of the solid products obtained after different synthesis times for: (A) S0.6; (B) S0.7; (C) S0.8; (D) S0.9; (E) S1.2; and (F) S2.0.
As shown in Figure 4(A) for S0.6, zeolite P was found to be absent by XRD as synthesis time was reduced to 30 h. However, the XRD results also indicated the presence of appreciable amounts of amorphous material. Hence, it was not possible to obtain well-crystallized FAU zeolite for composition S0.6. The same behavior was observed for S0.7 (Figure 4(B)), for which 28 h was the optimal time to avoid the presence of zeolite P. FAU zeolite, free from zeolite P and amorphous material, was obtained when synthesis time was to 15 h for S0.8 (Fig. 4(C)). Reducing time to 13h, 6h and 6h for syntheses S0.9, S1.2 and S2.0, respectively, prevented the formation of zeolite P and resulted in FAU-type zeolite with high crystallinity as the only product, as shown in Fig. 4(D), Fig. 4(E) and Fig.4 (F), respectively.

Table 3 gives the SiO$_2$/Al$_2$O$_3$ ratio in the FAU crystals determined by X-ray diffraction for the different Na$_2$O/SiO$_2$ ratios in the synthesis mixture and as a function of synthesis time. For each synthesis except S0.6, the observed values are constant within deviations of ±0.2, which was found to be the precision of the method by reproducing the same synthesis several times. As shown above, after an optimal synthesis time, zeolite P appeared in all cases and the FAU particles started to dissolve. Therefore, the nucleation of zeolite P and subsequent dissolution of FAU-zeolite resulted in a rather constant measured SiO$_2$/Al$_2$O$_3$ ratio in the dissolving FAU crystals, except for S0.6 which showed a strong decrease of this parameter along with dissolution of the FAU crystals. This suggests that the core of the FAU crystals is Al-rich in S0.6. This has already been observed experimentally on large FAU-crystals by energy dispersive spectroscopy [36] or on Ce$^{3+}$ exchanged zeolite Y by X-ray photoelectron spectroscopy [37].
Table 3. SiO$_2$/Al$_2$O$_3$ composition determined by XRD of the FAU products from optimal synthesis time and further on.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na$_2$O/SiO$_2$</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6h</td>
</tr>
<tr>
<td>S0.6</td>
<td>0.6</td>
<td>5.3</td>
</tr>
<tr>
<td>S0.7</td>
<td>0.7</td>
<td>4.7</td>
</tr>
<tr>
<td>S0.8</td>
<td>0.8</td>
<td>4.1</td>
</tr>
<tr>
<td>S0.9</td>
<td>0.9</td>
<td>3.9</td>
</tr>
<tr>
<td>S1.2</td>
<td>1.2</td>
<td>3.0</td>
</tr>
<tr>
<td>S2.0</td>
<td>2.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

3.3 Characteristics of the final product

Figure 5 shows scanning electron micrographs of all samples obtained after optimal synthesis time. All samples contained euhedral particles consisting of more or less intergrown crystals with octahedral symmetry. Particle size clearly increased as alkalinity was decreased by lowering the Na$_2$O/SiO$_2$ ratio from 2.0 to 0.7 (Fig.5(A) to Fig.5(E)), specifically from 0.5 µm for S2.0-6h to 2.3 µm for S0.7-28h. The degree of intergrowth also clearly diminishes with lowering the Na$_2$O/SiO$_2$ ratio in the same range. The crystals in S2.0-6h are irregular due to strong intergrowth, while increasingly more well-defined crystals with octahedral symmetry formed as the Na$_2$O/SiO$_2$ ratio was progressively decreased. However, particle size was found to decrease and the degree of intergrowth to increase again for S0.6-30h (Fig.5(F)), which corresponds to the lowest investigated Na$_2$O/SiO$_2$ ratio that led to the formation of FAU zeolite. For the Na$_2$O/SiO$_2$ ratio less than or equal to 0.8, the presence of unreacted materials becomes obvious (Fig.5(D) to Fig.5(F)). Large non-reacted diatomite skeletons are still present in S0.6-30h.
Figure 5. Scanning electron micrographs of (A) S2.0-6h; (B) S1.2-6h; (C) S0.9-13h; (D) S0.8-15h;
(E) S0.7-28h; (F) S0.6-30h.
4. Discussion

Table 4 shows yield in terms of silicon ($\eta_{Si}$) and aluminum ($\eta_{Al}$) calculated from gravimetric measurements and ICP-SFMS. Interestingly, both types of yield are fairly constant for all samples after optimal synthesis time. Yield in terms of silicon varies between 0.34 and 0.41 with no clear trend with regard to dependency on the $Na_2O/SiO_2$ ratio, while the values expressed on the basis of aluminum oscillates around 1, between 0.87 and 1.36. This strongly indicates that all aluminum introduced in the synthesis mixture is present in the final solid product, since the variations around 1 are within the margin of error of ICP-SFMS. On the other hand, the rather constant amount of silicon in the final product, independent of alkalinity, is not yet clearly understood.

The $SiO_2/Al_2O_3$ ratios of the final products determined by ICP-SFMS ($R_{ICP}$ in Table 4) were corrected by assuming 100% yield with respect to aluminum in the following way:

$$R_{ICP}^* = R_{ICP} \times \eta_{Al}$$  (1)

The corrected $SiO_2/Al_2O_3$ ratios are denoted $R_{ICP}^*$ in Table 4. The $R_{ICP}^*/R_{start}$ ratio gives, as expected, the overall yield in solid product with respect to silica determined by ICP-SFMS and gravimetrically, according to equation (2):

$$R_{ICP}^*/R_{start} = \frac{\eta_{SiO_2 \text{ final product}}}{\eta_{Al_2O_3 \text{ final product}}} \times \frac{\eta_{SiO_2 \text{ start}}}{\eta_{Al_2O_3 \text{ start}}} = \frac{\eta_{SiO_2 \text{ final product}}}{\eta_{SiO_2 \text{ start}}}$$  (2)

Although the overall yields with respect to silica are rather constant, the amount of zeolite produced depends strongly on alkalinity. The amount of FAU zeolite produced can be roughly estimated from the measured microporosity yield and X-ray crystallinity, which are reported in comparison to the values obtained for a commercial zeolite Y powder. Both values are reported in Table 4 (for selected samples free of zeolite P) and differ from one another by 15-30% with the microporosity yield values being higher than those for X-ray crystallinity for $Na_2O/SiO_2$ ratios >0.7. This is not surprising since part of the unreacted material can be microporous. On the other hand, it is well known that the sensitivity of X-ray diffractions is a few per cent for detecting one phase within another [38].
Therefore, the actual yield of FAU zeolite can be expected to lie somewhere in-between these two values. High values of the microporosity yield and X-ray crystallinity were obtained for Na₂O/SiO₂ ratios between 0.9 and 2.0, which shows that FAU crystals could be produced from diatomite at a high yield. However, these values dropped dramatically as alkalinity was decreased for Na₂O/SiO₂ ratios below 0.9. As shown above, fragments of diatomite were still present in the S0.6-30h sample, which clearly indicates that alkalinity was insufficient to digest the raw materials for Na₂O/SiO₂ ratios below 0.9.

Table 4. Yield, SiO₂/Al₂O₃ ratios and comparison of the latter for all best syntheses.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield in terms of Si (g)</th>
<th>Yield in terms of Al (g)</th>
<th>Starting SiO₂/Al₂O₃ ratio (R₀)</th>
<th>ICP-SFMS SiO₂/Al₂O₃ ratio (Rₑ)</th>
<th>ICP-SFMS SiO₂/Al₂O₃ ratio (Rₑ⁺⁺)</th>
<th>XRD SiO₂/Al₂O₃ ratio (Rₓrd)</th>
<th>XRD SiO₂/Al₂O₃ ratio (Rₓrd⁺⁺)</th>
<th>Microporous yield</th>
<th>X-ray crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0.6 - 30h</td>
<td>0.41</td>
<td>0.97</td>
<td>11.05</td>
<td>4.7</td>
<td>4.5</td>
<td>5.3</td>
<td>1.17</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>S0.7 - 28h</td>
<td>0.35</td>
<td>0.92</td>
<td>11.05</td>
<td>4.3</td>
<td>3.9</td>
<td>0.35</td>
<td>4.7</td>
<td>1.21</td>
<td>0.09</td>
</tr>
<tr>
<td>S0.8 - 15h</td>
<td>0.37</td>
<td>0.99</td>
<td>11.05</td>
<td>4.2</td>
<td>4.1</td>
<td>0.37</td>
<td>4.6</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>S0.9 - 13h</td>
<td>0.34</td>
<td>0.87</td>
<td>11.05</td>
<td>4.4</td>
<td>3.8</td>
<td>0.34</td>
<td>3.9</td>
<td>1.02</td>
<td>1.03</td>
</tr>
<tr>
<td>S1.2 - 6h</td>
<td>0.37</td>
<td>1.13</td>
<td>11.05</td>
<td>3.6</td>
<td>4.1</td>
<td>0.37</td>
<td>3.0</td>
<td>0.73</td>
<td>0.83</td>
</tr>
<tr>
<td>S2.0 - 6h</td>
<td>0.38</td>
<td>1.36</td>
<td>11.66</td>
<td>3.3</td>
<td>4.4</td>
<td>0.38</td>
<td>3.4</td>
<td>0.76</td>
<td>0.89</td>
</tr>
<tr>
<td>zY com</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
<td>5.2</td>
<td>-</td>
<td>5.2</td>
<td>0.99</td>
<td>1.00</td>
</tr>
</tbody>
</table>

By comparing the SiO₂/Al₂O₃ ratio in the zeolite, determined by XRD, with the corrected ICP-SFMS SiO₂/Al₂O₃ ratio in the final product (Rₓrd/Rₑ⁺⁺ values in Table 4), it is evident that the unreacted solid is Al-rich in S0.6-30h and S0.7-28h, while both the unreacted solid and the zeolite have approximately similar SiO₂/Al₂O₃ ratios for S0.8-15h and S0.9-13h. Increasing alkalinity further causes Rₓrd/Rₑ⁺⁺ values to drop below 1, which indicates that the unreacted solid must be Si-rich. In fact, Rₓrd/Rₑ⁺⁺ can be expressed in terms of moles as follows:

\[
R_{\text{XRD}}/R_{\text{ICP}⁺⁺} = \frac{n_{\text{SiO}_2 \text{ zeolite}}}{n_{\text{Al}_2\text{O}_3 \text{ zeolite}}} \times \frac{n_{\text{SiO}_2 \text{ final product}}}{n_{\text{Al}_2\text{O}_3 \text{ final product}}} \times \frac{n_{\text{Al}_2\text{O}_3 \text{ zeolite}}}{n_{\text{SiO}_2 \text{ final product}}} \times \frac{n_{\text{Al}_2\text{O}_3 \text{ final product}}}{n_{\text{SiO}_2 \text{ zeolite}}} = 3
\]
The last factor in eq. (3) must be larger or equal to 1. If all the aluminum in the final product is located in the zeolite, this factor is equal to 1 and \( R_{\text{XRD}}/R_{\text{ICP}} \) represents the zeolite yield with respect to silica in the solid product. The values of \( R_{\text{XRD}}/R_{\text{ICP}} \) of 0.73 and 0.76 obtained for S1.2-6h and S2.0-6h, respectively, lie in between the corresponding values of XRD crystallinity and microporous yield. This indicates that most of the aluminum, if not all, is located in the zeolite in the final products obtained for compositions S1.2 and S2.0 after 6h. For the other syntheses, the presence of aluminum in the unreacted product causes the last factor in eq. (3) to become larger than 1 and therefore \( R_{\text{XRD}}/R_{\text{ICP}} \) cannot be interpreted as the zeolite yield.

Two conclusions can be drawn from these results: (i) S1.2-6h and S2.0-6h produced FAU crystals with 100% yield with regard to the aluminum initially introduced; (ii) since 6h was the longest allowed synthesis time for obtaining FAU zeolite as the sole product for both compositions, it can be concluded that it is the depletion in aluminum that triggered the formation of zeolite P in these two cases. Depletion in aluminum supply and onset of the growth of zeolite P might also be compatible with the other investigated compositions. As a matter of fact, the apparent \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio measured by XRD clearly decreased as the FAU crystals started to dissolve and zeolite P began to grow (Table 3), indicating that less aluminum was included in the latest stages of growth of the FAU crystals before onset of dissolution. It is well known that aluminum is preferentially consumed over silicon in the beginning of the growth of FAU zeolites and that growth ceases as aluminum is depleted, which renders the synthesis of high silica faujasite difficult. This is usually assigned to the fact that aluminate ions are necessary for the formation of sodalite cages, which are part of the FAU structure [39]. However, although highly suspected and despite several attempts [40], a clear relationship between the growth rate of FAU crystals and the concentration of aluminate ions has never been established.

The \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio in the zeolite (\( R_{\text{XRD}} \) in Table 4) increased steadily as alkalinity decreased in our system using diatomite as silica source. In fact, it is well-known that low alkalinity conditions are required to synthesize high silica faujasite, since it has been shown by different research groups that the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio increases in various zeolites as the excess alkalinity decreases [41, 42]. It was proposed by Lechert et al. [42] that this stems from the fact that aluminate ions \( \text{Al(OH)}_4^- \) only react
with =Si-O' end groups and that the amount of the latter is directly related to alkalinity. Another explanation might be less incorporation of aluminum as sodium concentration decreases, since the former causes charge deficiency in the zeolite network which needs to be compensated by the latter [43].

However, this increase in silica content in the zeolite with decreasing alkalinity might appear contradictory at first, since less silica could obviously be liberated from diatomite as the Na₂O/SiO₂ ratio was diminished. Slow liberation of silica from diatomite is supported by the increase in size of the FAU crystals as alkalinity was reduced, which suggests fewer nucleation events and therefore decreasing supersaturation conditions, as does the slow dissolution of bulk silica like quartz during the formation of very large zeolite crystals [44]. Less liberation of silica species from diatomite at low alkalinity was also confirmed by preliminary results obtained by gravimetric analysis and ICP-SFMS, which indicates that 11% and 0.5% of all silicon introduced was present in the supernatant after centrifugation of the synthesis mixture after 24 h aging for composition S2.0 and S0.6. In contrast, the supernatant contained approximately 50% of all aluminum introduced for both compositions, which certainly originates from aluminum sulfate, since the latter represented 75% of all aluminum introduced in the synthesis. This high availability of aluminate ions before hydrothermal treatment shows that aluminate shortage cannot be held as responsible for the formation of FAU crystals with high SiO₂/Al₂O₃ ratio at low alkalinity.

Interestingly, the synthesis of high silica faujasite usually requires the use of colloidal silica as silica source, since FAU crystals with SiO₂/Al₂O₃ ratios larger than 3.9 cannot be obtained in the SiO₂-Al₂O₃-Na₂O-H₂O system by utilizing sodium silicate [3]. The use of diatomite also allowed SiO₂/Al₂O₃ ratios larger than 3.9 to be reached in the compositional field identified for colloidal silica by Breck and Flanigen (see Figure 2). Both silica sources are similar, in that they both have a higher degree of polymerization of silica than sodium silicates. Hence, our results show that the higher polymerized state of silica in colloidal silica and diatomite undoubtedly plays a role in the formation of high silica faujasite. It might be due to the release of larger silica species [42] or by further decrease of alkalinity during depolymerization of the starting silica source [45], or a mixture thereof. However,
diatomite was too bulky to be completely consumed under the investigated synthesis conditions. Further investigation of our system with diatomite is under way in order to understand the formation and growth of silica-rich FAU crystals. This knowledge is required if new strategies for the synthesis of high silica faujasite without the use of expensive colloidal silica or organic compounds such as tetraethylammonium hydroxide [46] or crown ethers [44] are to be found.

According to Breck and Flanigen’s definition, zeolite X is formed when the faujasite structure contains aluminum such as the SiO₂/Al₂O₃ ratio is below 3 [3]. This definition was confirmed by Rüscher et al. who argued that both domains of zeolite X and Y exist above this ratio and that pure zeolite Y can only be claimed if ratio is greater than or equal to 5.4 [39]. This delimitation was based on the resistance against amorphization during dealumination by steaming. In light of these definitions, all final products obtained in this work can be denominated zeolite Y. However, syntheses S2.0-6h and S1.2-6h produced FAU crystals with SiO₂/Al₂O₃ ratios close to 3 (see Table 4), which therefore can be said to mainly consist of zeolite X with very few zeolite Y domains. Lowering the Na₂O/SiO₂ ratio was not sufficient to produce pure zeolite Y, since synthesis S0.6-30h produced crystals with an average SiO₂/Al₂O₃ ratio of 5.3 (Table 4), but with an aluminum gradient (Table 3) and in low yield. However, both Breck and Flanigen’s and Rüscher’s studies showed that crystals with a SiO₂/Al₂O₃ ratio higher than 3.8 could present hydrothermal stability only inferior by approximately 10% to that obtained for high-silica zeolite Y after steaming at 410°C for 3 h or 500°C for 5 h, respectively. Therefore, the product of synthesis S0.9-13h, which showed a SiO₂/Al₂O₃ ratio of 3.9 and high crystallinity, may be a stable and inexpensive alternative for FCC catalysts.

5. Conclusions

In this study, it was shown that Bolivian diatomite from the Potosi region could be used as silica-rich source for the synthesis of zeolite Y. The diatomite was leached with sulfuric acid to remove impurities and aluminum sulfate was used to adjust the SiO₂/Al₂O₃ ratio to within the range of well-established syntheses. The raw materials were reacted hydrothermally at 373 K in water with sodium hydroxide and different Na₂O/SiO₂ ratios were investigated. After optimization of synthesis time,
zeolite Y with low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio (3.0-3.4), 100% yield in terms of aluminum and low amount of extraneous material was obtained at high alkalinity (Na\textsubscript{2}O/SiO\textsubscript{2} = 1.2-2.0). Decreasing alkalinity resulted in an increase of the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio in zeolite Y. However, high zeolite yield could only be achieved down to a Na\textsubscript{2}O/SiO\textsubscript{2} ratio of 0.9, which produced zeolite Y with a SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 3.9. Lower Na\textsubscript{2}O/SiO\textsubscript{2} ratios resulted in incomplete dissolution of diatomite and poor zeolite yield. Nevertheless, it was possible to synthesize almost pure zeolite Y with a SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 5.3 in low yield at a Na\textsubscript{2}O/SiO\textsubscript{2} ratio of 0.6. In this respect, diatomite behaved similarly to colloidal silica in traditional syntheses, with both sources of silica having a high degree of polymerization. Finally, overrun of all investigated compositions resulted in the formation of zeolite P nucleating and growing onto dissolving zeolite Y crystals, which was shown to be triggered when aluminum was completely depleted at high alkalinity.

6. Acknowledgments

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7. References

Paper II

Preparation of zeolite A with excellent optical properties from clay

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Preparation of zeolite A with excellent optical properties from clay

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Abstract

Discoloration of zeolite A powder is a common problem when natural raw materials such as kaolin clay are used because of the formation of colored iron compounds. In this study, we report on a novel method to produce zeolite A with excellent optical properties, from clays. The brightness is as high as 94.5 and the yellowness is as low as 3.0. The product is comprised of intergrown zeolite A crystals with cubic habit and a length ranging between 0.5 and 2 µm. Good optical properties are obtained when the raw material contains magnesium, as some natural raw materials do, or alternatively, when a magnesium compound is added to the raw material. Magnesium probably forces iron inside colorless extraneous magnesium aluminosilica compounds. This simple process appears very promising for the preparation of zeolite A with good optical properties from inexpensive natural raw materials.

Keywords:
Zelite A, clay, optical properties, iron, magnesium
1. Introduction

Zeolite A, LTA (Linde Type A) or 4A is a synthetic sodium aluminosilicate. It is a low silica zeolite represented by the formula: Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·27H₂O. The crystal structure is cubic with a lattice parameter of 12.32 Å. Zeolite A is characterized by a 3-dimensional network consisting of spherical cavities of 11.4 Å in diameter separated by circular openings of 4.2 Å in diameter [1]. It has a high cation exchange capacity as each alumina tetrahedral in the framework introduces a negative charge that must be compensated by a cation. This property confers to zeolite A water softening abilities by ion exchanging Ca²⁺ and to a lesser extent Mg²⁺ for Na⁺, thereby preventing precipitation of calcium compounds. Therefore, the most important application of zeolite A is as a detergent builder [2, 3].

For zeolite to be used as a detergent grade builder, there are various requirements set on the size of the particles, crystal shape, cation exchange capacity (CEC) and brightness. The optimal range for particle size is 1-10 µm [4]. Crystal sizes smaller than 1 µm may be retained in damaged textile fibers, while particles over 10 µm in size cause unacceptable deposition in textile materials, fabric and machine parts [5]. Incrustation of textiles can be reduced by achieving appropriate morphology of the crystals. Zeolite A crystals with sharp edges can be entangled in textile fibers. In contrast, zeolite A with rounded corners and edges tend to decrease incrustation on textile materials. Besides, the CEC of detergent builders must be as high as possible with 510 meqCa²⁺/100g of anhydrous solid being a recommended minimum [6] and 592 meqCa²⁺/100g the highest achievable value at 294.1 K and 1000 ppm [7]. Another important property of a detergent builder is the optical brightness which has to be at least 90% of the ISO reflectance measured on BaSO₄ or MgO.

Pure chemical grade reagents are mostly used to produce materials which fulfill all the aforementioned requirements. Concerns about energy consumption, carbon economy and production costs have called the attention of researchers to seek cheaper raw materials for zeolite synthesis [8, 9]. Many studies have been published on the synthesis of zeolite A from raw materials such as kaolin, diatomite, bentonite, fly ash, or smectite [10-14]. Kaolin is of particular interest because it possesses the appropriate SiO₂/Al₂O₃ ratio that matches the composition of zeolite A [15]. However, kaolin must be activated in the form of metakaolin by calcination at high temperature in the range 773-
1273K in order to produce an amorphous material that can be easily digested during zeolite synthesis [16].

The properties of zeolite A produced from metakaolin in terms of CEC, particle size and morphology were found to be adequate for use as detergent builder. However, problems associated with brightness and yellowness and related to the iron content are usually encountered when using kaolin for zeolite production [17, 18]. Various techniques for removal of iron have been investigated [19] such as selective flocculation [20, 21], magnetic separation [22, 23], acid leaching [24, 25], optimum temperature for metakaolinization [17] and chemical removal treatments [26]. As an example, Chandrasekhar [19] managed to reduce the amount of Fe$_2$O$_3$ in the final zeolite product from 0.59% to 0.04% starting with a Chinese kaolin containing 0.69 % Fe$_2$O$_3$ by a combination of treatments, i.e. clay refining, control of alkali concentration, complexing and washing with alkaline water. Dramatic improvement of the optical properties of the final zeolite A product were observed, the brightness increased from 72.9 to 81.7% and yellowness reduced from 11.5% to 7.8%. However, these separation procedures represent additional costs to the general process.

Use of other types of clays than kaolin as raw materials for the synthesis of zeolite A might result in brightness improvement. However, natural clays based on 2:1 phyllosilicate clays usually contain quartz and do not produce a reactive product such as metakaolin upon calcination. The energy used for the metakaolinization heat treatment can be used with advantage to fuse raw materials containing quartz under the action of the sodium required for zeolite synthesis. It is known that through alkali activation, large amounts of aluminosilicates can be transformed into more soluble species [27].

In this study, we report on a novel method to improve brightness in zeolite A prepared by alkali fusion from natural clays, namely Bolivian montmorillonite and commercial kaolinite clays.

2. Experimental Section

2.1 Materials

Montmorillonite-type clay sampled from the Rio Mulatos zone (Potosi, Bolivia) and commercial kaolin (Riedel de Haën, pro analysis) were used as aluminosilica sources. Sodium hydroxide was
employed in the form of pellets (NaOH, Sigma Aldrich, p.a., ≥98%). Anhydrous sodium aluminate in powder form (NaAlO₂, Riedel-de Haën, p.a., Al₂O₃ 50 – 56 %, Na₂O 40-45 %) was used to adjust the SiO₂/Al₂O₃ ratio to that of typical synthesis mixtures for zeolite A. Calcium nitrate (Ca(NO₃)₂·4H₂O, Merck) and magnesium nitrate (Mg(NO₃)₂·6H₂O, Merck) were utilized to investigate the influence of Ca and Mg on the color properties of alkali-activated kaolin, while ion exchange was carried out with sodium nitrate (NaNO₃, Merck). Commercial zeolite A powder (Akzo Nobel) was used as a reference. Barium sulfate (BaSO₄, Sigma Aldrich, p.a. 99%) was used as a standard for brightness and yellowness measurements.

2.2 Synthesis procedure

The initial SiO₂/Al₂O₃ molar ratio of the Rio Mulatos clay (RMA) was 4.9 (see Table 1). Hence an additional amount of sodium aluminate was required to decrease this ratio to the proper value. NaAlO₂ and NaOH provided the aluminum and sodium to set both the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios to 2. RMA clay was added to sodium aluminate and sodium hydroxide in calculated proportions and the mixture was carefully crushed in an agate mortar until a homogeneous powder was obtained. The crushed powder was placed in a platinum crucible and heated at 873 K for 1 hour using a heating rate of 10 K/min. The resultant mixture was crushed again, dispersed in distilled water and stirred for 6 h in an aging step. In the case of kaolin (KFA), the same procedure was used without the addition of sodium aluminate. The molar ratio of the components in the mixtures was SiO₂/Al₂O₃ = X, Na₂O/SiO₂ = 2 and H₂O/Na₂O = 40 with X varying between 2.0 and 1.15. After the aging period, the reaction mixture was transferred to Teflon-lined autoclaves and heated at 373 K for different times in order to perform optimization of the hydrothermal treatment. Subsequently, the autoclave was quenched in cold water to stop the reaction. The solid products were repeatedly washed and filtered in distilled water until pH in the filtrate liquid reached 8-9. The products were dried at 373 K overnight. The prepared samples were denoted according to the type of clay that was used, namely RMA or KFA, followed with the molar SiO₂/Al₂O₃ ratio within brackets and synthesis time, e.g. RMA(2.0)-3h corresponded to a sample obtained from a mixture with a molar SiO₂/Al₂O₃ ratio of 2.0 using Rio Mulatos clay after 3 h of synthesis.
2.3 Apparatus

To determine the chemical composition of the clays, fused clays and synthetic zeolite products, inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) was used. For the analysis, 0.1 g sample was digested with 0.375 g of LiBO₂ and dissolved in HNO₃; LOI (loss on ignition) was performed at 1273 K. The mineralogical composition of the raw materials and products were determined by X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer, CuKα1 radiation with λ = 1.540598 Å at 45 kV and 40 mA in the range of 2θ = 5-50° at a scanning speed of 0.026°/s. The peaks observed in the diffractograms were compared with the existing pattern of known materials from the powder diffraction files (PDF). The morphology of the raw materials, intermediate products and final products were studied by extreme high resolution-scanning electron microscopy (XHR-SEM Magellan 400, the FEI Company) at low accelerating voltage without conductive coating.

Energy dispersive spectroscopy (EDS, X-max detector 50 mm², Oxford Instruments) was also performed to establish the overall composition of the final products and to gain compositional information about individual zeolite A crystals and extraneous phases. EDS analysis was carried out at 10 kV on a SEM equipped with a microinjector (Merlin SEM, Carl Zeiss) in order to mitigate charging by blowing nitrogen gas close to the surface of samples. The concentration of Na, Mg, Al and Si was measured at low magnification (100 times) to avoid diffusion of Na, while the concentration of Ca was measured locally in 10 individual crystals. Brightness and yellowness were measured on a spectrometer using an integrating sphere (Perkin Elmer Lambda 2SUV/VIS). The results were expressed in percentage of the reflectance obtained for the Ba₂SO₄ powder [28]. Brightness was measured at 457 nm, while the difference between the reflectance measured at 570 and 457 nm yielded a measure for yellowness.

The number of equivalents-gram was calculated for Ca²⁺ in each case. The total exchange equivalents for Ca²⁺ was assessed by subtracting the amount of equivalents of Ca²⁺ present for the initial to the final number of equivalents of Ca²⁺ after the exchanged process.
3. Results

3.1 Synthesis of zeolite A by alkali fusion

The diffractogram of the raw RMA clay (Figure 1A) shows the characteristic peaks of montmorillonite at 2θ = 5.9, 19.8 and 35° as compared with PDF patterns, but also the occurrence of quartz in low content. Raw kaolin (KFA in Figure 1C) contains mostly kaolinite as evidenced by reflections at 2θ = 12.33; 19.80; 20.40; 21.40; 24.81 and 35.11, but also traces of quartz and muscovite (2θ = 8.83; 35.06). The elemental compositions of the RMA and KFA clays obtained by ICP-SFMS are given in Table 1. Apart from silica and alumina, calcium and magnesium were present in appreciable amounts in the Bolivian montmorillonite in comparison to kaolin. However, both clays contained similar amounts of iron, i.e. 0.79-0.82 wt. % Fe₂O₃.

### Table 1. Main components of the raw materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂ (wt. %)</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>K₂O</th>
<th>MgO</th>
<th>LOI</th>
<th>SiO₂/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMA</td>
<td>63.75</td>
<td>21.95</td>
<td>0.82</td>
<td>0.71</td>
<td>3.19</td>
<td>0.46</td>
<td>4.64</td>
<td>7.20</td>
<td>4.90</td>
</tr>
<tr>
<td>KFA</td>
<td>54.43</td>
<td>42.87</td>
<td>0.79</td>
<td>0.13</td>
<td>0.07</td>
<td>1.41</td>
<td>0.30</td>
<td>12.20</td>
<td>2.20</td>
</tr>
</tbody>
</table>

During alkali fusion at 873 K, montmorillonite and quartz, as well as kaolin, suffered a structural reorganization. Fused RMA and fused KFA resulted in formation of various sodium aluminosilicates, i.e. Na₂SiO₃, Na₂Al₂O₄, Na₃Al₅Si₃O₁₄, etc. as evidenced by XRD data shown in Fig.1B and Fig.1D. All compounds formed after alkali fusion of the starting clays could be readily dissolved in water and serve as reactants for zeolite synthesis in combination with sodium aluminate and sodium hydroxide.
Figure 1. XRD diffractograms of: (A) RMA; (B) fused RMA; (C) KFA and (D) fused KFA.

Figure 2 shows the XRD diffractograms of the final products after hydrothermal treatment at 373 K after different synthesis times. When a molar SiO$_2$/Al$_2$O$_3$ ratio of two was used, 3 and 4 hours of hydrothermal treatment was required to obtain zeolite A as a unique product with high crystallinity for the RMA and KFA clays, respectively (RMA(2.0)-3h and KFA(2.0)-4h in Figure 2). Samples obtained after shorter synthesis times still contained appreciable amounts of amorphous material (RMA(2.0)-2h and KFA(2.0)-3h in Figure 2). Table 2 shows the overall SiO$_2$/Al$_2$O$_3$ ratios of the final products determined by EDS. RMA(2.0)-3h was found to contain an excess of silica with a SiO$_2$/Al$_2$O$_3$ ratio of 2.36 compared to the ideal ratio of 2.0 in terms of cation exchange capacity. Therefore, the molar SiO$_2$/Al$_2$O$_3$ ratio in the RMA synthesis mixture was varied in the range 1.15-2.0. Decreasing this ratio from 2 to 1.8 resulted in a slight decrease of the SiO$_2$/Al$_2$O$_3$ ratio in the product to 2.22, see RMA(1.8)-3h in Table 2 and also Figure 2. However, it was not possible to lower the ratio in the product further by increasing the amount of aluminum in the synthesis mixture. Instead, this resulted in a steady decrease in crystal size, while the SiO$_2$/Al$_2$O$_3$ ratio in the product was almost
constant. The RMA sample prepared with a molar SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of 1.8 were also mainly amorphous for synthesis times shorter than 3 h, e.g. RMA(1.8)-2h in Figure 2.

**Figure 2.** XRD diffractograms of the RMA(2.0)-2h; RMA(2.0)-3h; RMA(1.8)-2h; RMA(1.8)-3h; KFA(2.0)-3h and KFA(2.0)-4 samples.

**Table 2.** Compositional ratios in the final products determined by EDS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion exchange</th>
<th>SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</th>
<th>Na/Al</th>
<th>2Ca/Al</th>
<th>2Mg/Al</th>
<th>(Na+2Ca)/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>commercial</td>
<td>-</td>
<td>2.08</td>
<td>0.99</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.99</td>
</tr>
<tr>
<td>RMA(2.0)-3h</td>
<td>-</td>
<td>2.36</td>
<td>0.87</td>
<td>0.11</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>-</td>
<td>2.22</td>
<td>0.90</td>
<td>0.12</td>
<td>0.19</td>
<td>1.02</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>Na</td>
<td>2.28</td>
<td>0.93</td>
<td>0.03</td>
<td>0.18</td>
<td>0.96</td>
</tr>
<tr>
<td>KFA(2.0)-4h</td>
<td>-</td>
<td>2.22</td>
<td>0.97</td>
<td>0.01</td>
<td>0.01</td>
<td>0.98</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>-</td>
<td>2.16</td>
<td>0.99</td>
<td>n.d.</td>
<td>0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>Na</td>
<td>2.28</td>
<td>0.98</td>
<td>0.01</td>
<td>0.16</td>
<td>0.99</td>
</tr>
</tbody>
</table>

n. d. (non-detected)
3.2 Size and morphology of the particles

Figure 3 shows SEM micrographs of RMA(1.8)-3h, KFA(2.0)-4h and the commercial powder.

Figure 3. SEM micrographs of: (A)-(B) RMA(1.8)-3; (C)-(D) KFA(2.0)-4; (E)-(F) commercial zeolite A.
As shown in Fig. 3 (A), RMA(1.8)-3h consisted of cubic crystals ranging between 0.5-1.5\(\mu\)m in length. Part of the crystals exhibited intergrowth, which is usually rationalized by a high concentration of nuclei [29]. Fig. 3(B) reveals that the largest crystals possessed chamfered edges, which is suitable for detergent grade zeolites. The zeolite crystals of the KFA(2.0)-4 sample showed similar characteristics, except for a slight increase in length to approximately 1-2 \(\mu\)m (Fig. 3(C) and Fig. 3(D)). Comparatively, the crystals in the commercial powder were found to measure between 1 and 7 \(\mu\)m in length (Fig. 3(E)) and to be relatively intergrown (Fig. 3(F)).

3.3 Brightness measurements

Table 3 shows the results of the brightness and yellowness measurements which were performed on RMA(1.8)-3h, KFA(2.0)-4h and the commercial powder. With 94.5% brightness and 3.0% yellowness, the sample obtained from Rio Mulatos clay after optimal synthesis time (RMA(1.8)-3h) showed excellent optical properties. These values were superior to those of the commercial powder, which exhibited 92.6% brightness and 3.8% yellowness. In comparison, the sample produced from commercial kaolin was found to exhibit a slight orange color to the naked eye. This was confirmed by the poor brightness and relatively high yellowness values obtained for KFA(2.0)-4h in Table 3, i.e. 76.4% and 14.4%, respectively. These values are typical of zeolite A powder synthesized from metakaolin. Therefore, the method to activate kaolin did not seem to influence the final color of the zeolite A powder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness</th>
<th>Yellowness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial powder</td>
<td>92.6</td>
<td>3.8</td>
</tr>
<tr>
<td>RMA(1.8)-3h</td>
<td>94.5</td>
<td>3.04</td>
</tr>
<tr>
<td>KFA(2.0)-4h</td>
<td>76.4</td>
<td>14.4</td>
</tr>
<tr>
<td>KFA(2.0)Ca-4h</td>
<td>73.7</td>
<td>11.5</td>
</tr>
<tr>
<td>KFA(2.0)Mg-4h</td>
<td>82.1</td>
<td>5.4</td>
</tr>
<tr>
<td>KFA(2.0)MgCa-4h</td>
<td>85.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>
3.4 Cation Exchange Capacity

As shown in Table 2, the commercial zeolite A and KFA(2.0)-4h samples were completely in sodium form, as evidenced by the Na/Al ratios which were estimated to be 0.99 and 0.97, respectively. However, the as synthesized samples obtained by alkali fusion of Rio Mulatos clay were not completely in sodium form but also contained calcium ions that occupied approximately 11-12% of the sites. With regard to cation exchange capacity (CEC), 84% of the exchangeable sites of zeolite A can be compensated by Ca$^{2+}$ cations at 294 K, which represents 592 meq Ca$^{2+}$/100g anhydrous solid. Considering the final SiO$_2$/Al$_2$O$_3$ and 2Ca/Al ratios measured on the RMA(2.0)-3h and RMA(1.8)-3h samples by EDS, maximum CEC values of 480-487 meq Ca$^{2+}$/100g anhydrous solid could be anticipated for these samples. As a matter of fact, loss-on-ignition and ICP-SFMS measurements on the calcium ion exchanged RMA(2.0)-3h sample yielded a value of 487 meq Ca$^{2+}$/100g anhydrous solid. The RMA(1.8)-3h sample was ion exchanged with sodium nitrate to verify that the calcium ions were exchangeable. As shown in Table 2, the 2Ca/Al ratio was reduced from 0.12 to 0.03, which showed that this is the case.

It is noteworthy that all samples investigated in Table 2 showed (Na+2Ca)/Al ratios very close to 1.0 in Table 2. This reflects the validity of the quantitative EDS method developed in this work. It was indeed found to be more reliable than ICP-SFMS because of the large error margin of the latter, which brought too much uncertainty on the elements present in large amounts.

4. Discussion

Usually, the poor brightness and yellowness of zeolite A powders synthesized from kaolin are attributed to formation of colored iron precipitates (e.g. iron(III) hydroxide) during the aging step and the crystallization process [30]. The iron content was found to be 0.44 and 0.54 wt. % by ICP-SFMS in the RMA(1.8)-3h and KFA(2.0)-4h samples, respectively. Although these amounts were similar and both samples were synthesized by the same method, the corresponding final zeolite products showed very different optical properties in terms of brightness and yellowness.
Referring to Table 1, the major compositional difference between the two raw materials investigated in this work was the high content in calcium and magnesium in Rio Mulatos clay. These elements were still present in appreciable amounts in the final products as shown by the EDS results in Table 2. Therefore, the difference in optical properties was first attributed to a positive effect of one of these (or both) elements. In order to test this hypothesis, amounts of calcium and magnesium similar to those present in RMA clay were added to the synthesis mixture based on KFA clay before alkali fusion using nitrates. Three new products were obtained and denoted KFA(2.0)Ca-4h, KFA(2.0)Mg-4h and KFA(2.0)MgCa-4h depending on whether only calcium or magnesium or both elements were added, respectively. All final products consisted mostly of zeolite A with minor contents of sodalite (~5%). The results in Table 3 showed that the addition of solely calcium slightly improved yellowness. Interestingly, addition of magnesium to kaolin before alkali fusion remarkably enhanced the optical properties of the final powder, independently of whether calcium was added or not. The corresponding brightness and yellowness values were higher than those obtained by Chandrasekhar and colleagues [19] who employed a complex combination of chemical treatments to reduce the amount of Fe$_2$O$_3$ in the final zeolite product to 0.04 wt.%.

The results in Table 2 indicated that, in contrast to calcium, magnesium was not ion-exchanged by sodium when exposed to a solution of sodium nitrate, which was consistent with the fact that solvated magnesium ions can barely diffuse into zeolite A. In addition, the fact that all values of the (Na+2Ca)/Al ratio were close to 1 strongly suggested that magnesium was not located inside zeolite A. As a matter of fact, Mg could not be detected by local EDS inside zeolite A crystals. This is illustrated by the EDS spectrum of Fig. 4(B), which was obtained by point analysis in a zeolite A crystal, i.e. the encircled region in Fig. 4(A). Instead, Mg and Fe were found to be concentrated in the extraneous material consisting of platelets and finely divided matter as revealed in the region delimited by the rectangle in Fig.4(A) and the corresponding EDS spectrum in Fig.4(C). Consequently, our data strongly suggest that magnesium exerts a masking effect on iron by incorporating the latter inside magnesium aluminosilica compounds with low coloration. This simple method appears as a promising alternative to complex and costly techniques developed in order to
reduce the iron content in natural raw materials.

![SEM micrograph of extraneous matter of RMA(1.8)-3h; EDS analysis](image)

**Figure 4.** (A) SEM micrograph of extraneous matter of RMA(1.8)-3h; EDS analysis of (B) Extraneous matter (dotted square in A) and (C) Zeolite A crystal (dotted circle in A).

5. Conclusions

Zeolite A crystals were successfully synthesized from Bolivian montmorillonite type clay and commercial kaolinite using the alkali fusion method. The crystals had cubic habit with a length ranging between 0.5 and 2 µm and intergrown. Although Bolivian montmorillonite and commercial kaolinite contained similar concentration of iron, they radically differed in terms of optical properties. This was attributed to the magnesium present in the Bolivian raw material, which probably forced iron inside colorless extraneous magnesium aluminosilica compounds. The effect was verified by
addition of magnesium to kaolinite. This simple process appears very promising to prepare zeolite A with excellent optical properties from inexpensive natural raw materials.

6. Acknowledgments

The financial support by the Swedish Institute in the SIDA Program is acknowledged. Financial support from Bio4energy is also acknowledged. The authors also wish to thank The Knut and Alice Wallenberg Foundation for financial support with the Magellan SEM instrument.

7. References

Paper III

Comparison between leached metakaolin and leached diatomaceous earth as raw materials for the synthesis of ZSM-5

Wilson Aguilar-Mamani, Gustavo García, Jonas Hedlund and Johanne Mouzon

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Comparison between leached metakaolin and leached diatomaceous earth as raw materials for the synthesis of ZSM-5

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ABSTRACT

Inexpensive raw materials have been used to prepare ZSM-5 zeolites with SiO₂/Al₂O₃ ratios in the range 20 – 40. Kaolin or Bolivian diatomaceous earth was used as aluminosilicate raw materials and sodium hydroxide and n-butylamine were used as mineralizing agents and template. Dealumination of the raw materials by acid leaching made it possible to reach appropriate SiO₂/Al₂O₃ ratios and to reduce the amount of iron and other impurities. After mixing the components and aging, hydrothermal treatment was carried out and the products were recovered. The results clearly show for the first time that well-crystallized ZSM-5 can be directly prepared from leached metakaolin or leached diatomaceous earth using sodium hydroxide and n-butylamine as mineralizing agents and template under appropriate synthesis conditions. A longer induction time prior to crystallization was observed for reaction mixtures prepared from leached diatomaceous earth, probably due to slower digestion of the fossilized
diatom skeletons as compared with that for microporous leached metakaolin. The use of leached diatomaceous earth allowed higher yield of ZSM-5 crystals within comparable synthesis times. However, low amounts of Mordenite formed, which was related to the high calcium content of diatomaceous earth. Another considerable advantage of diatomaceous earth over kaolin is that diatomaceous earth does not require heat treatment at high temperature for metakaolinization.

Keywords: Kaolin; diatomaceous earth; n-butylamine; ZSM-5 zeolite

1. Introduction

The zeolite ZSM-5 (Zeolites Socony Mobil) is an aluminosilicate with high silica ratio with suitable properties for catalysis, adsorption and membrane applications [1-3]. Researchers [4] of Mobil Oil Corporation obtained the first patent on the synthesis of ZSM-5 zeolite, in which they described that this zeolite can be formed with ratios of SiO$_2$/Al$_2$O$_3$ varying between 20 and 120. Depending on this ratio, the acidity and surface properties of ZSM-5 vary and therefore it is important to carefully control this parameter in the final product [5, 6].

Typical syntheses of ZSM-5 require sources of silicon and aluminium, a mineralizer (e.g. OH$^-$ or F$^-$) and an organic molecule as templating agent. Quaternary ammonium compounds like tetrapropyl ammonium bromide (TPA-Br) [6, 7] and tetrapropyl ammonium hydroxide (TPA-OH) [8] are mostly used for the synthesis of ZSM-5. Unfortunately, these quaternary ammonium compounds are rather expensive. The molecule n-butylamine was reported [9-12] as an alternative templating agent to replace TPA-Br and TPA-OH and is about 100 times less expensive on a molar basis. In the past two decades, efforts have also been undertaken to identify inexpensive Si and Al sources to synthesize ZSM-5[13-16] and it has been shown
that kaolin clay and diatomaceous earth are two suitable and inexpensive sources of silica and alumina.

Kaolin clay contains kaolinite with a SiO$_2$/Al$_2$O$_3$ ratio close to 2 and therefore it is well suited for the preparation of low-silica zeolites such as zeolite A [17-20]. To obtain this zeolite from kaolin, two steps are necessary: first, a thermal treatment of kaolin to obtain an amorphous and reactive material denoted metakaolin. The second step is a hydrothermal treatment to convert metakaolin to zeolite in an alkaline aqueous medium. Preparation of zeolites with higher SiO$_2$/Al$_2$O$_3$ ratios such as zeolites X [21-23] and Y [24, 25] from kaolinite has also been reported. However, the syntheses of these zeolites require either an increase of the amount of silica or partial removal of aluminium. The first alternative implies using an additional source of silica with high solubility, e.g. sodium silicate. The second alternative, i.e. dealumination, consists in either leaching kaolin in a solution of an inorganic acid (HCl, H$_2$SO$_4$, HNO$_3$) [26] or alternatively calcining the kaolin with an inorganic acid (H$_2$SO$_4$) [27, 28].

The synthesis of ZSM-5 zeolite from kaolin with additional sources of silica has been reported in patent [29] and research papers [30, 31]. Dealumination of metakaolinite to synthesize ZSM-5 has also been investigated [32]; [33]; [34]. In all these studies, expensive tetrapropylamine was used as template. The synthesis of ZSM-5 with a high SiO$_2$/Al$_2$O$_3$ ratio from metakaolin and silica sol and less expensive $n$-butylamine has been reported [11]. However, to the best of our knowledge, a combination of dealumination of metakaolin by acid treatment together with the use of $n$-butylamine as a template has not yet been reported.

Diatomaceous earth is another inexpensive source of silica, which is a sedimentary rock comprised of fossilized skeletal remains of diatoms. It consists essentially of amorphous hydrated silica and a small amount of alumina and also impurities such as iron [35]. It can be
used to produce mesoporous material such as MCM-41 [36] and also both low and high silica zeolites such as A [37], P [38] or NaP [39], analcime [40], [41], cancrinite [40], hydroxisodalite [40], NaY [42] and mordenite [35]. In most of these syntheses, the raw diatomaceous earth was acid treated to remove iron and other impurities. The conversion of diatomaceous earth to ZSM-5 was also studied in combination with other raw materials such as paper sludge ash [38] or volcanic ash [13]. However, there are a few studies on the synthesis of ZSM-5 by using only diatomaceous earth as silica source. In these studies, diethanolamine[16] and expensive tetrapropylammonium bromide [43] were used as templates and these synthesis required quite long crystallization times from 40 hours to 6 days at a quite high temperature of 180 °C.

In the present work, we show for the first time that leached metakaolinite or diatomaceous earth in combination with sodium hydroxide and \( n \)-butylamine can be used as inexpensive raw materials for the synthesis of ZSM-5 without using an additional source of silica. However, both sources of alumino-silica are shown to behave differently during the course of synthesis and to lead to slightly different reaction products. In particular, we discuss these discrepancies in terms of composition, morphology, and porosity of the raw materials.

2. Experimental

2.1 Raw materials

Kaolin (Riedel de Haen, pro analysi), diatomaceous earth (Murmuntani zone in the locality of Llica, Potosi, Bolivia), sodium hydroxide (Sigma Aldrich, reagent grade, \( \geq 98\% \), anhydrous pellets), \( n \)-butylamine (Sigma Aldrich, 99.5 %) and hydrochloric acid (Merk, pro analysi 37 %) were used as reagents.

2.2 Heat treatment
Kaolin was first calcined in a porcelain crucible that was placed in a furnace and heated at a rate of 8 °C/min in air. When the temperature reached 750 °C, this temperature was maintained for 2 h to obtain metakaolin and the temperature in the furnace was then reduced to room temperature. It was not necessary to carry out the heat treatment for the diatomaceous earth in order to obtain ZSM-5, and consequently, this material was not heat treated. On the other hand, if the heat treatment of kaolin was omitted, no zeolite formed.

2.3 Dealumination of raw materials

Metakaolin and diatomaceous earth were acid leached in a spherical glass container under reflux conditions in a thermostated oil bath maintained at 115 °C. Metakaolin or diatomaceous earth was stirred in hydrochloric acid (3 M) for 150 minutes. The metakaolin or diatomaceous earth to acid weight ratio was 1:17. Subsequently, the suspension was quenched and the acid leached product was washed with distilled water. Finally, the product was separated by filtration and the filter cake was washed with distilled water until the pH reached a value close to 7.

2.4 Hydrothermal synthesis

The synthesis mixtures were prepared by mixing the aluminosilicate sources with distilled water, n-butylamine (NBA) and sodium hydroxide. The molar ratios in the synthesis mixtures were: Na₂O/SiO₂ = 0.18; SiO₂/Al₂O₃ = X; SiO₂/NBA = 7; H₂O/SiO₂ = 30, where X = 33 and 44 for leached metakaolin and leached diatomaceous earth, respectively. The mixtures were aged under stirring for 24 hours at room temperature and were thereafter hydrothermally heated in Teflon lined stainless steel autoclaves kept for different times in an oil bath at 165 °C. After hydrothermal treatment, the solids were recovered by filtration and washed with
distilled water until the pH reached a value close to 7. The powders were dried at 100 °C overnight and finally calcined at 550 °C for 6 hours to remove the template.

2.5 Characterization of the products

The chemical compositions of kaolin, diatomaceous earth, leached aluminosilicates and the final products were determined using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). Samples of 0.1 g were fused with 0.4 g of LiBO₂ and dissolved in HNO₃. Crystallinity was examined by X-ray diffractometry (XRD) using a PANalytical Empyrean X-ray Diffractometer equipped with Cu LFF HR X-ray tube, a graphite monochromator, and a PIXcel3D detector. The X-ray tube was operated at 30 mA and 40 kV. The investigated 2θ range was from 5 to 50° with a step size of 0.026°. The degree of crystallinity was calculated by using the area of characteristic peaks of ZSM-5 between 22 and 25° after background removal following the equation by van Hooff [44].

ZSM-5 crystals with an average length of 10 µm synthesized from silicic acid and TPAOH by following the method reported by Lechert and Kleinwort [45] were used as standard.

The morphology of the ZSM-5 crystals was studied by scanning electron microscopy (SEM, Magellan 400, FEI Company) without coating. The chemical composition of individual crystals was determined by energy dispersive spectrometry (EDS, 80 mm² X-max detector, Oxford Instruments) at an accelerating voltage of 10 kV. Nitrogen adsorption-desorption data were recorded with an ASAP 2010 equipment from Micrometrics to determine the BET specific surface area, total pore volume and micropore volume of the raw materials and reaction products, as well as the reference crystals. The weight percentage of solid retentate after aging was determined by filtration through a 1 µm filter paper and gravimetric method, while the filtrates were analyzed by ICP-SFMS.
3. Results

3.1 Characterization of the starting materials

X-ray diffractograms of the raw aluminosilicates and dealuminated counterparts are shown in Figure 1. Kaolin of course contains mostly kaolinite (evidenced by reflections at $2\theta = 12.33; 19.80; 20.40; 21.40. 24.81$ and $35.11$) but also traces of quartz ($2\theta = 20.85; 26.66$) and muscovite ($2\theta = 8.83; 35.06$). Kaolin after calcination and leaching was mostly an amorphous material with weak characteristic peaks of muscovite and quartz. On the other hand, raw diatomaceous earth shows the occurrence of halite NaCl ($2\theta = 27.41; 31.76; 45.53$), muscovite ($2\theta = 8.83; 27.83; 35.06$ ), albite ($2\theta = 22.03; 23.70$) and quartz ($2\theta = 20.85; 26.66$) in addition to amorphous material. After acid treatment and the subsequent washing, the amorphous material remained and NaCl was removed, but the other minor constituents were still present (muscovite, albite and quartz).

Figure 1. XRD diffractograms of the raw materials and acid-leached materials
The chemical compositions of the raw and leached materials measured by ICP-SFMS are given in Table 1. Raw kaolin and diatomaceous earth had a SiO$_2$/Al$_2$O$_3$ ratio of 2.2 and 15, respectively. This ratio was successfully increased by acid leaching to 33 and 44 for kaolin and diatomaceous earth, respectively. Acid leaching also reduced significantly the concentration of impurities in both materials. Finally, the leached materials had comparable compositions in terms of magnesium, potassium and iron. However, leached diatomaceous earth was approximately 4 times richer in sodium and calcium, which can be understood from the presence of NaCl and calcium carbonate in the raw diatomaceous earth originating from a region close the salt lake Uyuni.

Table 1. Compositions (in mole %) of kaolin, diatomaceous earth, leached metakaolin, leached diatomaceous earth and ZSM-5 products by ICP-SFMS.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Kaolin</th>
<th>Leached metakaolin</th>
<th>ZSM-5 (K)</th>
<th>Diatomaceous earth</th>
<th>Leached diatomaceous earth</th>
<th>ZSM-5 (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>67.7</td>
<td>95.9</td>
<td>94.0</td>
<td>78.8</td>
<td>96.4</td>
<td>96.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>30.1</td>
<td>2.92</td>
<td>4.15</td>
<td>5.22</td>
<td>2.17</td>
<td>2.40</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
<td>0.12</td>
<td>0.10</td>
<td>4.44</td>
<td>0.49</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.37</td>
<td>0.16</td>
<td>0.18</td>
<td>0.22</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.13</td>
<td>0.60</td>
<td>0.65</td>
<td>1.29</td>
<td>0.33</td>
<td>0.30</td>
</tr>
<tr>
<td>MgO</td>
<td>0.59</td>
<td>0.19</td>
<td>0.22</td>
<td>3.30</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.16</td>
<td>0.08</td>
<td>0.65</td>
<td>6.78</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Mol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$/Al$_2$O$_3$</td>
<td>2.2</td>
<td>33</td>
<td>23</td>
<td>15</td>
<td>44</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 2 shows the morphology of the raw materials and leached materials revealed by SEM. Kaolin is composed of stacks of platelets with hexagonal symmetry which is typical of natural kaolinite (Fig 2(a)). The leached metakaolin (Fig. 2(b)) has very similar platelet morphology but the surface area increased from 12 to 288 m$^2$/g as presented in Table 2. This is not surprising since acid-leached metakolin is known to form microporous silica [34]; [33]. Raw diatomaceous earth (Fig. 2(d)) exhibited large particles with typical shapes of diatomaceous biogenic sediments. Some diatomaceous earth particles were partially broken in smaller
pieces by the mechanical action of stirring during the acid treatment but their characteristic shapes could still be distinguished (Fig. 2(e)). Leaching of diatomaceous earth only caused a slight increase in specific surface area (from 38 to 55 m$^2$/g; Table 2).

Figure 2. SEM images of: a) kaolin, b) leached metakaolin (LMK). c) solid part of LMK after aging, d) diatomaceous earth, e) leached diatomaceous earth (LD) and f) solid part of LD after aging.
Table 2. Surface area and pore volumes derived from nitrogen adsorption data for the raw, leached materials, final products and standard sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
<th>Micropore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>12</td>
<td>0.058</td>
<td>0.004</td>
</tr>
<tr>
<td>Leached Metakaolin</td>
<td>288</td>
<td>0.24</td>
<td>0.089</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>38</td>
<td>0.093</td>
<td>0.003</td>
</tr>
<tr>
<td>Leached Diatomaceous earth</td>
<td>55</td>
<td>0.11</td>
<td>0.006</td>
</tr>
<tr>
<td>ZSM-5 (K)</td>
<td>255 (82%)</td>
<td>0.17</td>
<td>0.082 (68%)</td>
</tr>
<tr>
<td>ZSM-5 (D)</td>
<td>298 (96%)</td>
<td>0.15</td>
<td>0.098 (82%)</td>
</tr>
<tr>
<td>ZSM-5 standard</td>
<td>310</td>
<td>0.15</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.2 Hydrothermal synthesis

Hydrothermal synthesis in terms of composition of the synthesis mixture and synthesis time was first optimized to maximize the yield of ZSM-5 using leached metakaolin as a raw material. The composition used in this work was found to produce the highest yield of ZSM-5 crystals. Figure 3 shows the evolution of XRD crystallinity compared with a reference sample composed of 6-10 µm ZSM-5 crystals. It can be noticed in Fig. 3(a) that samples prepared from leached metakaolin reached maximum crystallinity for synthesis times between 9 and 12 hours before decreasing for prolonged hydrothermal treatments. The reaction parameters of the dealumination and hydrothermal treatments obtained on kaolin were employed for diatomaceous earth. As shown in Fig. 3(b), the best crystallinity for leached diatomaceous earth was obtained for 12 hours of synthesis.
3.3 Characterization of the crystalline products

The diffractograms of the final reaction products obtained from both types of raw materials after 12 h synthesis are presented in Figure 4. The main characteristic peaks correspond to the MFI structure ($2\theta = 7.9; 8.7; 23.0$ etc.) in good agreement with the reference pattern PDF-042-0024. The intensities of the main peak of quartz are similar in both samples and of the same order of magnitude as in the leached materials. Therefore, the quartz content is similar in both samples and originates from the raw materials. However, the reaction product obtained from diatomaceous earth contained traces of mordenite, approximately 5% of the intensity of the main peak of ZSM-5. The composition of the final products after 12 h synthesis was determined by ICP-SFMS analysis and the results were presented in Table 1. The average SiO$_2$/Al$_2$O$_3$ ratio was 23 and 40 for the reaction products obtained from leached metakaolin and diatomaceous earth, respectively. From these data, the reaction products could
be considered as quite pure ZSM-5 with traces of mordenite formed during synthesis and of quartz remaining from the raw material.

Figure 4. XRD diffractograms of the products obtained after 12 h of synthesis from: (a) leached metakaolin; (b) leached diatomaceous earth.

The morphology of the reaction products was studied by SEM and typical images were presented in Figure 5. Synthesis from leached metakaolin resulted in the formation of flat tablet shaped ZSM-5 crystals with a diameter of 5-6 µm, but also some smaller particles, as shown in Fig. 5 (a). In contrast, the ZSM-5 crystals obtained from leached diatomaceous earth were rounded with average diameter around 7-8 µm and aspect ratio close to 1 (Fig. 5(b)). This sample also contained smaller particles and particularly small slabs as those encircled in Fig. 5(b), which were attributed to mordenite.
4. Discussion

As shown above, the combination of both sodium hydroxide and \textit{n}-butylamine together with leached metakaolin or leached diatomaceous earth was efficient to produce micron-sized ZSM-5 crystals within similar synthesis times. However, the reaction mechanism seems to differ depending on which alumino-silica source was used. Fig. 3(a) clearly shows that crystal growth is triggered after an induction period of 2 h and slowly progresses until maximum crystallinity is reached after 9 h when leached metakaolin was used. In contrast, the induction period was extended to 6 h before a sudden burst of crystal growth occurred between 8 and 9 h, if leached diatomaceous earth was used as alumino-silica source (Fig. 3(b)). The differences in growth rates are not yet understood. However, the difference in induction period between both synthesis mixtures may be related to the state of the synthesis mixtures after 24h aging and before hydrothermal treatment. After filtration through a 1-µm filter paper, 26 and 80 wt% of the original solid material remained from the aged synthesis mixtures prepared from leached metakaolin and leached diatomaceous earth, respectively. The filtrates were found to be silica-rich sols by ICP-SFMS (\text{SiO}_2/\text{Al}_2\text{O}_3 \text{ ratio} \sim 400-800). As shown in Fig.2(c), the solid retentate of the aged synthesis mixture prepared from leached
metakaolin consisted of poorly defined platelets with a SiO$_2$/Al$_2$O$_3$ ratio of 7.5, which probably stem from undigested muscovite or other materials that did not become microporous or possibly sintered upon calcination. On the other hand in Fig.2(f), particles with typical morphology of fossilized diatom still comprised the main constituent of the diatomaceous earth synthesis mixture after aging, even though further comminution occurred by mechanical mixing during aging. Therefore, the longer induction time encountered for the leached diatomaceous earth system can be imparted to the heavily condensed state still present after aging in comparison to the silica-rich sol resulting from aging of the leached metakaolin mixture, the latter being more homogeneous and requiring less transformation for nucleation of zeolite crystals.

Although induction time was longer, the maximum crystallinity was slightly higher for samples prepared from diatomaceous earth than from kaolin and amounts to 93 and 87%, respectively, as shown in Fig. 3. By a normalization of the BET specific surface area and total micropore volume with respect to the ZSM-5 standard sample also used for determining crystallinity by XRD, we show that the crystallinity of the reaction product obtained from kaolin is in good agreement with the values given in Table 2 with a specific surface area of 82%. The total micropore volume (68%) value indicates that the final product prepared from kaolin contains approximately 30% of non-microporous material in addition to the ZSM-5 crystals. The same values calculated from the BET specific surface area and total micropore volume for the diatomaceous earth-derived product, 96 and 82% respectively, are higher than that obtained by XRD (93%). This can be attributed to the presence of mordenite as a by-product in addition to non-microporous materials.

It was not possible to prevent the formation of mordenite by further optimization of the synthesis parameters. Instead, formation of mordenite occurred randomly, probably due to the
variability of the diatomaceous earth raw material. Calcium was found to be concentrated in
the mordenite crystals as revealed by the comparison of the EDS spectra between uncalcined
ZSM-5 (Fig. 6(a)) and mordenite (Fig. 6(b)) crystals. Therefore, the higher calcium content in
leached diatomaceous earth as compared to leached kaolin probably favored the formation of
mordenite. The presence of $n$-butylamine as templating agent in the ZSM-5 crystals was also
confirmed by EDS, as shown in Fig.6(a) with the characteristic peak of nitrogen and carbon,
while that of sodium was quite weak.

The BET specific surface area obtained in this work for the sample prepared from leached
diatomaceous earth (298 m$^2$/g) is comparable with that obtained in the study by Sang et al. 9
(294 m$^2$/g), who employed water glass and aluminum sulfate as Si and Al sources,
respectively. Therefore, Bolivian diatomaceous earth appears as a competitive source of
inexpensive raw materials for the synthesis of ZSM-5 crystals. In addition to the higher
crystallinity and BET specific surface area achieved in this work compared with kaolin,
diatomaceous earth does not require heat treatment at high temperature for metakaolinization.

![Figure 6. EDS spectra of: (a) a ZSM-5 crystal and (b) a mordenite crystal in the final product
obtained from leached diatomaceous earth after 12 h synthesis.](image)
5. Conclusions

The inexpensive raw materials: kaolin, Bolivian diatomaceous earth, sodium hydroxide and \(n\)-butylamine have been used to prepare ZSM-5 zeolites with \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratios in the range 20 – 40. Dealumination of the raw materials by acid leaching made it possible to reach appropriate \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratios and to reduce the amount of iron and other impurities in the raw materials. After mixing and aging for 24 hours, synthesis by hydrothermal treatment was carried out at 165 °C either using leached metakaolin or leached diatomaceous earth as source of alumino-silica. The results clearly show for the first time that well-crystallized ZSM-5 can be directly prepared from both materials in combination with sodium hydroxide and \(n\)-butylamine under appropriate synthesis conditions. Reaction mixtures prepared from leached diatomaceous earth showed longer induction period due to the slower digestion of the fossilized diatom skeletons compared with microporous leached metakaolin. However, the use of leached diatomaceous earth allowed higher yield in ZSM-5 crystals within comparable synthesis times despite the formation of low contents of mordenite, which was related to the high calcium content of diatomaceous earth. Another considerable advantage of diatomaceous earth over kaolin is that diatomaceous earth does not require heat treatment at high temperature for metakaolinization.

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