

Synthesis and characterization of the DDR type zeolite

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ABSTRACT

Separation of light gases by adsorption is considered to be one of the promising applications of zeolite membranes. DDR type zeolites possessing extremely fine pore structure are regarded as good candidates to be utilized for this purpose. In order to prepare a membrane using a seeding technique, small seed crystals should be available. For the moment very few methods of DDR type zeolites synthesis exist and limited amount of publications describing their properties are to be found.

In this work, DDR type zeolite crystals syntheses were performed according to the methods described by den Exter et al. and claimed in the patents by A. Stewart and K. Nakayama et al. The samples obtained in this work were characterized by XRD, SEM, BET, FT-IR and FT-Raman spectroscopy.

DD3R clathrasil crystals were successfully synthesized following the procedure suggested by den Exter et al. when seeding with Sigma-1 seed crystals. But this method might be considered quite inconvenient owing to long synthesis time (25 days) and stirring required in order to get pure DD3R clathrasil.

The method of DD3R film preparation claimed by K. Nakayama was considered to be not suitable for DD3R crystals synthesis since we were not able to reproduce the results reported in the patent.

The procedure of Sigma-1 crystals synthesis claimed by A. Stewart was found to be simple and although the sample obtained was partially amorphous, it was of sufficient quality to be used as seed crystals in DD3R synthesis. It was noticed that proper stirring was required in order to get uniformly sized and shaped crystals.

X-ray diffraction was used for samples identification complemented by FT-Raman and FT-IR spectroscopy. Crystal size and morphology were investigated using scanning electron microscopy. All the mentioned techniques allowed revealing impurities and evaluating an approximate degree of crystallinity of the samples obtained. Finally, pore structure and sorption properties were studied by means of nitrogen adsorption/desorption measurements.

Key words: DD3R, clathrasil, Sigma-1, zeolite, gas separation, molecular sieve.

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1 INTRODUCTION

1.1 Background

Gas separation is of extreme importance in refinery, chemical and petrochemical industries. Distillation, extraction and sorption processes are widely used for this purpose nowadays but they require a lot of energy and are often quite complicated to carry out. Application of membranes for the purpose of gas separation is regarded as an environmentally friendly, economically reasonable and simple process [1]. In addition to low energy consumption, membrane separations allow continuous operation that makes their application even more attractive. Membranes are usually classified as organic or inorganic. Application of organic polymer membranes is limited by their low thermal and chemical stability. Lately, molecular-sieve inorganic membranes have been a subject to extensive research due to their ability to stand high temperatures and aggressive media [1, 2].

Microporous zeolites of different structure types are used for membrane preparation. Their pores vary in size affecting both their adsorptive and molecular sieving properties [3]. In order to increase the selectivity of a membrane separation process it is important that the pore diameter of the membrane is nearly of the same size as the molecules that are to be separated [1]. One of the possible applications of molecular-sieve zeolite membranes is the separation of carbon dioxide (CO_2) and methane (CH_4), which are molecules of almost the same size. The mixture of CH_4 and CO_2 may for example originate from anaerobic treatment of biomass or natural gas production. CH_4 can be used as a fuel if CO_2 is removed. Different types of zeolites with medium and large pores have been tested for CO_2/CH_4 separation but their pore apertures seem to be too large to provide high selectivity. On the contrary all-silica zeolite deca-dodecasil 3R (DD3R) possessing smaller pores is reported to be a good candidate for this application [1, 2, 4].

1.2 Scope of the present work

The scope of the present work was to prepare DD3R type zeolite crystals according to previously reported methods [2, 5, 6]. A further objective was to characterize the crystals using X-ray diffraction (XRD), scanning electron microscopy (SEM), gas adsorption (BET), Fourier Transform Infra Red and Raman spectroscopy (FT-IR and FT-Raman).

2 THEORY

2.1 Zeolites

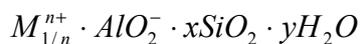
2.1.1 General description

According to the classification suggested by Liebau et al. [7, 8], porous tectosilicates (or in other words framework silicates) can be divided into two groups: zeolites and clathrasils. The main differences between them are their alumina content. Clathrasil can also be referred to as all-silica zeolite.

The Swedish mineralogist A. F. Cronstedt in 1756 was the first to observe that steam was released from a mineral called stilbite when heated. And it was he who introduced the term “zeolite,” comprised of the Greek “*zeo*” for boil and “*lithos*” for stone. Since then about 40 kinds of such natural minerals have been discovered [9].

The first attempts to prepare zeolite synthetically were made more than a century ago. The first claim to have succeeded was made by St. Claire Deville in 1862 when he obtained a zeolite named levynite [10]. Nowadays more than 170 zeolite structure types are known [11], most of them have no natural analogues.

Today zeolites are understood as crystalline microporous tectoaluminosilicates with uniformly sized pores and cavities of molecular dimensions [9]. They possess a three-dimensional framework built of corner-sharing $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. All the oxygen atoms are shared between tetrahedra giving the ratio of the total aluminum and silicon atoms to oxygen atoms 1:2. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a counterion [12]. The chemical composition of zeolites may be expressed as:



where M – counterion (can be a metal cation, an ammonium or an alkylammonium cation); n – counterion valency; x – silicon/aluminum ratio ≥ 1 ; y – content of hydrate water [13].

The non-framework metal cations within the channels can be substituted for other cations thus giving the zeolite its ion-exchange properties. By means of cation exchange it becomes possible to vary the properties of the given zeolite by suitable selection of the cation. In the case of that a hydrogen ion is used as a cation, the zeolite gains acid-catalytic properties. Zeolites have different crystal structures that determine the pore diameters, which in known zeolites varies between ca 0.3 and 1 nm [13]. Cavities and pores are uniform in size within a specific zeolite material and thus

permit only molecules of certain size and shape to penetrate inside the channels and reject those of larger dimensions [12]. This type of separation is termed molecular sieving [14].

Clathrasils are all-silica clathrate compounds with 3-dimensional frameworks built of $[\text{SiO}_4]^{4-}$ tetrahedra linked in the corners with cage-like voids in-between [15]. The framework types DDR, DOH, MEP and MTN belong to the clathrasil family and can be built using units that consist of 30 T-atoms (T stands for Si or Al). These T30-units can be connected in a periodic manner in 2-dimensions to form hexagonal layers. Deca-dodecasils 3R (DD3R) can be considered as a link between zeolites and clathrasils because it possesses zeolitic properties through a clathrasil structure. Due to this fact it is often referred to as DD3R zeolite.

The Structure Commission of the International Zeolite Association has assigned three letter structure type codes to all zeolites of known structure. Frequently, different names have been assigned to materials having the same structure type but a composition different from the material which was the basis for the original assignment of the structure type code (type material). Such materials are referred to as isotypes [11]. Zeolites of the DDR structure type include DD3R clathrasil, the type material, and three isotypes – zeolites ZSM-58, SSZ-28 and Sigma-1 [16].

2.1.2 DD3R clathrasil

The pioneering work on DD3R synthesis and determination of its structure was done by Gies [17, 18], a detailed description of the clathrasil DD3R structure is given in the literature [17].

The chemical composition of deca-dodecasil 3R can be represented as $[(\text{C}_{10}\text{H}_{17}\text{N})_6 (\text{N}_2)_9] [\text{Si}_{120}\text{O}_{240}]$, where $\text{C}_{10}\text{H}_{17}\text{N}$ is 1-aminoadamantane (Figure 1) used as a template molecule in the synthesis.

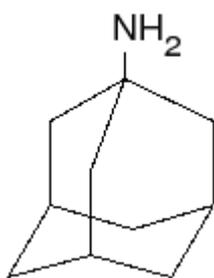


Figure 1. 1-aminoadamantane [19].

DD3R possesses trigonal crystal structure with the following cell parameters: $a = 13.860$, $b = 13.860$, $c = 40.891 \text{ \AA}$, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$ in hexagonal settings [11]. Trigonal structure is often considered to be a subdivision of the hexagonal system because rhombohedral crystals can always be described in terms of hexagonal axes [20]. The crystal structure is built of $[\text{SiO}_4]^{4-}$

tetrahedra linked in the corners and sharing all oxygen atoms. The tetrahedra are connected into the rings of 4, 5, 6 and 8 Si atoms, which subsequently form three different cages: dodecahedron, decahedron and 19-hedron (Figure 2, a, b and c respectively). The latter is occupied by the 1-aminoadamantane template molecule during the synthesis. During calcination up to ca. 773 K, the template molecule is decomposed and removed from the crystalline structure, providing the clathrasil with zeolitic properties [15].

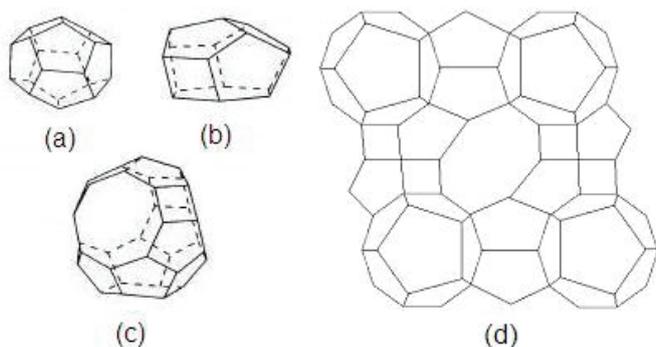


Figure 2. Basic cages of the all-silica DD3R zeolite [2].

Each 19-hedron cage is connected with three other cavities, placed in a hexagonal arrangement, through 8-membered rings with an aperture of 0.44x0.36 nm [1] forming a 2-dimensional pore system along [001] (Figure 2, d) [15].

DD3R clathrasil has a well-pronounced morphology of crystals shaped in the form of rhombohedra and is characterized by a distinctive XRD pattern and a unique IR spectrum to be found in the literature [2, 11]. The XRD pattern reveals quite a lot of peaks, which is typical for structures with rather low symmetry (as the trigonal structure). Peaks at low 2-theta values are evidence of a large unit cell.

2.1.3 Sigma-1 zeolite

Sigma-1 zeolite was first reported by A. Stewart, UK [6]. As stated previously, Sigma-1 zeolite have the DDR type structure. The same structure directing agent is used in the synthesis of Sigma-1 as in the synthesis of DD3R clathrasil (1-adamantanamine). But in contrast to DD3R, Sigma-1 contains both silicon and aluminium oxides. The formula of Sigma-1 can be represented as:



where M – monovalent inorganic cation or 1/n of a cation of valency n; X – silicon and/or germanium; Y – typically aluminum, but could, in principle, also be iron, chromium, titanium, vanadium, zirconium, molybdenum, arsenic, antimony, manganese, gallium and/or boron.

The crystalline form of Sigma-1 synthesized by Stewart [6] has Si/Al ratio around 60. Without an alumina source in the synthesis mixture, formation of all-silica Sigma-2 is observed. At Si/Al ratio equal to 30, formation of zeolite Nu-3 is favored. It was found that at high at high free OH/SiO₂ ratios α -quartz and α -cristobalite are formed as well as mordenite. At intermediate ratios ZSM-5 and α -cristobalite were formed. Sigma-1 particles are found in the form of rounded tablets, about 2.5 microns in diameter [21]. XRD data and IR-spectrum of Sigma-1 zeolite are available in the literature [6]. The XRD pattern of Sigma-1 is, as expected, very similar to that of DD3R clathrasil but the peaks are more splitted and have different relative intensities.

2.1.4 ZSM-58 zeolite

ZSM-58 zeolite is a zeolite with low aluminum content [22] and is another isotype of the DDR type zeolites first reported by E.W. Valyocsik, USA [12]. Its composition on an anhydrous basis can be expressed with the formula:



where M – alkali or alkaline earth metal cation of valency n; R – organic cation.

The structure directing agent is an organic N,N-dimethyltropinium ion (Figure 3) in the form of e.g. halide, hydroxide or sulphate salt.

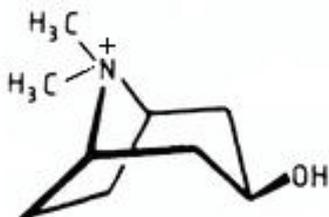


Figure 3. N,N-dimethyltropinium ion.

The Si/Al ratio in the as-synthesized material can vary between 50 and 1000. The reported crystals are of two habits: large (5-25 μ m) spherical and small rhombohedral (0.5-1 μ m) [22]. The latter are placed on the surface of larger crystals and are similar to those of DD3R clathrasil. The XRD pattern of ZSM-58 [12] is very similar to that of Sigma-1 zeolite but there are some additional peaks present and the relative intensities are slightly different.

2.1.5 SSZ-28 zeolite

SSZ-28 zeolite is yet another isotype of the DDR type zeolites that was synthesized by S.I. Zones, USA [23]. Its composition on an anhydrous basis can be expressed with the formula:



where M – alkali metal cation; Q – organic cation; Y – silicon and/or germanium; W – one or more of aluminum, iron, gallium and/or boron.

The organic cation, serving as template molecule, is a N,N-dimethyltropinium or N,N-dimethyl-3-azonium bicyclo[3.2.2]nonane cation in the form of e.g. halide, hydroxide, sulphate, acetate or carboxylate salt.

Si/Al ratio in the as-synthesized SSZ-28 can be between 20 and 45 [23].

2.1.6 Zeolite crystals synthesis

Zeolites are generally synthesized hydrothermally from a mixture containing suitable silica and alumina sources in a certain ratio, an alkali source as well as a structure directing agent (template). The role of the hydroxide anions is first to solubilize silica and alumina to silicate and aluminate anions respectively and then to facilitate the condensation of the formed anions to the zeolite framework [3]. The template molecule contributes to formation of a stable structure by means of the additional template-template or template-framework bonds introduced. Due to a templating effect, it leads to formation of a microporous structure by occupying the voids between tetrahedra [3].

The produced inhomogeneous gel gradually crystallizes sometimes forming several types of zeolite at the same time. The synthesis temperature is often between 100 and 200⁰C. The pressure is autogenous and is proportional to water content in the synthesis mixture. The final product is the result of a joint action of many factors including silica to alumina ratio and water content, temperature, aging, stirring, presence of a template etc. [14].

As-synthesized zeolites are usually calcined in order to remove water of crystallization and template molecules, opening the pore system. Subsequently, they may be subjected to ion-exchange in order to obtain the desired properties.

For the all-silica DD3R synthesis 1-aminoadamantane is used as a structure directing agent. In addition, silica source, water and ethylenediamine are added where the latter is used for increasing the solubility of the template. The formation of generally co-crystallizing clathrasil DOH is favored at temperatures >170⁰C and at high concentrations [2]. This can be avoided if the poorly soluble template is prevented to separate from the aqueous synthesis mixture. This is prevented by

adding the above mentioned ethylenediamine, using stirring of the synthesis mixture and using alkyl-containing silica sources e.g. tetraethylorthosilicate (TEOS) or tetrametoxysilane (TMOS), which when hydrolyzed, form ethanol or methanol, respectively, hence increasing the solubility of the template [2].

Synthesis procedures for DD3R type zeolites are described in the literature [2, 5, 6, 12].

2.1.7 Application of zeolites

Due to their high activity zeolites are widely used as acid catalysts in various acid-catalyzed reactions e.g. catalytic cracking of hydrocarbons, isomerization, methanol-to-gasoline process. If some of the aluminium atoms in the crystal structure are substituted for other metals (e.g. transition metals or noble metals) a catalyst with dual functionality can be obtained. It possesses two types of active sites – acid sites and hydrogenation-dehydrogenation sites – and can be used e.g. for isomerization and hydrocracking [3]. Another application of zeolites include drying and water softening, [14]. Physical adsorption of gases on microporous materials is an important subject that has received considerable attention in recent years, especially for the purpose of separation of hydrocarbons [15, 24]. The separation factors may be increased if the pore size of adsorbent matches the kinetic diameter of gas molecules. The all-silica DD3R with pore apertures of 0.36x0.44 nm formed by 8-atoms rings appears to be the most suitable material for the separation of methane and carbon dioxide [4, 5, 15], which have kinetic diameters of 0.38 and 0.33 nm respectively [25]. Furthermore, due to the absence of aluminium in the structure of DD3R, it possesses hydrophobic properties and interacts with water to a lesser extent compared to other zeolites [1]. Hydrophobicity allows it to retain its adsorption capacity when water present [26], thus making it a candidate for separating biogases which contain large amounts of moisture [4]. Moreover, a high silica to alumina ratio provides high temperature stability of the zeolite structure [14]. The pore aperture is small enough to exclude larger molecules like aromatics prolonging performance lifetimes by preventing coke formation and pore plugging [2].

Both Zhu et al. [15] and Ruthven et al. [27] reported high adsorption selectivity of DD3R for propene over propane. Tomita et al. [1], Himeno et al. [4] and den Exter et al. [2] reported it to show high adsorption selectivity for carbon dioxide over methane, and attributed thus to the molecular-sieving effect [1]. According to den Exter et al. alkanes and alkenes with 3 or more carbon atoms show slow adsorption on DD3R zeolite while branched molecules are excluded from the structure.

The hydrogen forms of Sigma-1, ZSM-58 and SSZ-28 zeolites can be used as acid catalysts, adsorbents and ion-exchangers.

2.2 Characterization methods

In order to be able to predict zeolite behaviour in different processes and efficiently utilize its unique properties it is extremely important to know its physical and chemical structure. Some standard methods of characterization include determination of total surface area, pore size distribution, plus certain mechanical properties. Some commonly used instrumental techniques for characterizing zeolite materials are SEM, XRD and IR spectroscopy [14].

2.2.1 X-ray diffractometry

This method can be used to gain information about the structure of a zeolite and to determine its unit cell dimension (and thus the zeolite framework composition, e.g. Si/Al ratio) and crystal size (by means of broadening measured at one-half the height of the peak, which is inversely proportional to crystallite size). XRD is of great importance in identification of prepared zeolites, by comparison to reference patterns. XRD can also provide information about the structure of amorphous or noncrystalline materials. If a crystalline and an amorphous materials of the same composition are analyzed with XRD the diffraction pattern of the crystalline sample shows a number of sharp peaks and the amorphous sample shows one broad peak centered in the range in which the strong peak was seen in the pattern of the crystalline material. The reason is that an amorphous material only exhibits short-range order in contrast to long-range order in a crystal [20]. In classical powder diffractometry the sample is exposed to a beam of X-rays and as a result we get the intensity of X-rays scattered by the atoms as a function of diffraction angle (2θ). Theta angle increases As the d-spacing within the crystals decreases reflections are observed at larger theta angles in accordance with Bragg's law, Equation 1 [20].

$$\lambda = 2d \cdot \sin \theta \quad (1)$$

where λ – wavelength of the incident radiation;

d – interplanar spacing;

θ – scattering angle.

The relative intensity of a certain reflection in the x-ray diffraction pattern is affected by the structure factor of the unit cell (which is independent of its shape and size), the multiplicity factor (which is dependent on crystal symmetry) and orientation of the crystals within the sample [3]. It is important that crystals, especially large ones, should be randomly orientated when powder analysis is carried out [20].

2.2.2 Scanning electron microscopy (SEM)

The scanning electron microscopy is used for recording images of a sample surface. The images are used for studying topology of surfaces as well as morphology and size of particles and crystals. By means of SEM characteristic three-dimensional images of the surface under observation with very high resolution (ca 1 nm) can be obtained.

In a SEM, electrons are emitted by an electron gun. The electron beam passes a series of lenses on its way to the sample and hits its surface. The incoming electron beam leads to several simultaneous effects used in various methods of surface characterization. Secondary electrons emitted from the sample are used to obtain SEM images. Backscattered electrons give topographical and atomic number information as well as information on crystallographic structure of the specimen. Characteristic x-radiation may be applied in electron-probe microanalysis and to determine distribution of elements within the sample [14].

In order for the electrons not to accumulate in a non-conducting specimen, coating with a thin gold layer is often necessary.

2.2.3 Fourier transform infrared and Raman spectroscopy

Both Raman and infrared spectroscopies are nondestructive and sensitive techniques using the interactions of the incident radiation with the sample material to obtain information about its bonding structure [28]. These techniques complement each other because different types of bonds are infrared and Raman active. For example, bonds with an existing dipole, such as C=O, are easily detected by infrared spectroscopy and, in contrast, homopolar bonds, such as N≡N, are infrared inactive but can be detected by Raman spectroscopy. A complete picture of sample's bonding structure can be obtained if both Raman and infrared spectroscopies are performed [29]. These techniques can, for instance, be used for the identification of prepared zeolites by means of comparing their characteristic spectroscopic peaks to existing reference spectra.

Two types of spectrometers exist: dispersive and Fourier Transform. The main advantage of FT spectrometers over the dispersive spectrometer is that all wavelengths are measured simultaneously in an interferogram making analysis much faster [30].

Infrared spectroscopy (IR spectroscopy) deals with the infrared region of the electromagnetic spectrum [31]. When the sample is exposed to IR radiation, a part of it may be absorbed by molecular vibrations and a part may be scattered. If radiation scattering is predominant over absorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) may be applied [3].

Raman spectroscopy is based on inelastic Raman scattering of a laser beam by the sample. The laser light interacts with the vibrations in the system, resulting in the energy shifting down or up (termed Stokes and anti-Stokes scattering respectively). The shift in energy gives information about the vibration modes [29].

In FT-Raman spectroscopy spectra are normally measured using an excitation source in the near infrared region. This usually reduces fluorescence from the sample and makes it relatively easy to measure at a much higher signal/noise ratio [29]. One more advantage is that sample preparation is very easy and doesn't require any mixing with other compounds that makes it possible to analyze samples available in very small amounts. The main disadvantage of the technique is that it is not as sensitive as infrared spectroscopy because it uses inelastically scattered radiation, which usually only appears in 0.1% of photons hitting the sample [29].

2.2.4 Brunauer-Emmett-Teller method

This method is used for determining the specific surface area and the pore size distribution of samples. The principle is to evaluate the volume of gas adsorbed on the surface of the zeolite as a function of relative pressure. The BET equation (2) [14] with certain assumptions describes multilayer adsorption:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (2)$$

where V – volume of gas adsorbed at pressure P

V_m – volume of gas adsorbed in monolayer

P_0 – saturation pressure of adsorbate gas at the experimental temperature

C – a constant related exponentially to the heats of adsorption and liquefaction of the gas

$$C = e^{(q_1 - q_L)/RT} \quad (3)$$

where q_1 – heat of adsorption on the first layer

q_L – heat of liquefaction of adsorbed gas on all other layers

R – the gas constant

$\frac{P}{V(P_0 - P)}$ is plotted versus P/P_0 and a straight line should be obtained with the slope S , equal to $(C - 1)/V_m C$ and the intercept I , equal to $1/V_m C$. Experimental data is mostly in very good agreement with BET equation over values of the relative pressure P/P_0 between approximately 0.05 and 0.3, and this range is usually used for surface area measurements. Microporous zeolites show a linear region in BET plot at low values of P/P_0 , typically around 0.01 or less. Zeolite micropores are essentially filled at $P/P_0=0.05$, adsorption at higher values mostly represents that in voids between crystals and also on external surfaces of the zeolite.

From Eq. (2), $V_m = 1/(S + I)$. The surface area of the zeolite can be calculated from V_m if the average area occupied by an adsorbed molecule is known.

According to the Brunauer classification [32], zeolite materials are characterized by Langmuir type adsorption isotherm (Type 1) that is common for microporous materials with relatively small external surface area. The amount of gas adsorbed increases rapidly at low partial pressures up to a limiting value corresponding to complete filling of the micropores.

Pore size distribution and microporosity can be investigated using the “t-plot” method, where nitrogen adsorption is plotted as a function of t , the thickness of the adsorbed layer inside the pores. Extrapolation of a t-plot to $t=0$ can yield the micropore volume. If the material contains mesopores, a hysteresis loop is usually observed which is the result of capillary condensation of adsorbate in the mesopores at the values of relative pressure higher than 0.30. In this case, pore size distribution can be determined using the desorption curve.

Any condensable inert vapour could in principle be used in the BET method, however small, inert and approximately spherical molecules are preferred. The vapour should be easy to handle at required temperatures in order to achieve the above stated values of relative pressure. Nitrogen and krypton are considered to be the best candidates for this purpose. The latter is used for the samples with small total surface areas [14].

3 EXPERIMENTAL

The most commonly used methods for preparation of DD3R clathrasil crystals is described by den Exter et al. [2]. In that method 1-aminoadamantane (1-ADA) prepared from 1-adamantanamine hydrochloride and sodium hydroxide was used as a structure directing agent. Following the above mentioned method, it was decided to prepare 1-ADA though it is commercially available.

3.1 1-aminoadamantane synthesis

The template molecule, 1-aminadamantane, used in the DD3R synthesis, was prepared according to the method described by den Exter [2]. The reagents used were sodium hydroxide p.a. (Merck, >99%) and 1-adamantanamine hydrochloride (Fluka, >99%). First, water solutions of the components were prepared and then mixed in equimolar amount. After that the mixture was extracted 3 times by diethyl ether (Riedel-de Haen). Finally, the solvent was removed by evaporation under vacuum and rotation until the residue was almost dry. The white coloured 1-adamantanamine was dried in the oven at 50⁰C and characterized by FT-IR and FT-Raman spectroscopy as well as XRD.

3.2 DD3R clathrasil crystals synthesis

Hydrothermal syntheses of DD3R crystals were performed according to the methods described by den Exter et al. [2] and Nakayama et al. [5] (Table 1). Synthesis solutions were prepared in teflon beakers using 1-ADA (both in-house prepared and purchased from Aldrich, 97%), ethylenediamine (Sigma-Aldrich), distilled water and different sources of silica: TMOS (Aldrich, 99+ %), TEOS (Merck, >98%), silica sol (Ludox, 30 wt. %, Aldrich).

According to the method described by K. Nakayama et al. [5], Example 4, the synthesis mixture was prepared as follows: in the first Teflon beaker, the 1-ADA was dissolved in ethylenediamine and subsequently put in a shaking machine for 30 minutes. In the other Teflon beaker, water and silica sol were gently stirred with a magnet stirrer for 30 minutes and then added to the 1-ADA mixture. The resulting was then vigorously stirred for 1 hour. Thereafter the solution was poured into a teflon lined stainless steel autoclave and subjected to heat treatment in a preheated oven at 160⁰C for 5 days.

The synthesis procedure described by den Exter et al. [2] comprised the following steps: 1-ADA was dissolved in ethylenediamine, water was added rapidly and the mixture was kept in a shaking

machine for one hour. After that the mixture was heated to 95°C and kept at this temperature for one hour while stirring. Then it was cooled down in ice and 6.42 g of the ice-cooled TMOS was added dropwise under vigorous stirring. Before filling the autoclave, the synthesis mixture was again heated to 95°C while stirring until it became almost clear. Then it was poured into a teflon lined stainless steel autoclave and subjected to heat treatment in an oil bath at 160°C under stirring at 150 rpm for 25 days.

When the synthesis was completed, the autoclave was cooled down to room temperature and discharged. The sediment formed in the autoclave was centrifuged for 30 minutes at 20000 rpm. Directly after centrifugation, the supernatant was discarded and the pellet was redispersed in distilled water. The centrifugation and redispersal were repeated 4 times. The pellet was subsequently dried in the oven at 50°C. Finally, the pellet was calcined in air for 5 hours at 700°C.

The obtained samples were investigated by FT-IR and FT-Raman spectroscopy, SEM and XRD.

Table 1. DD3R clathrasil syntheses.

Synthesis	Method	Ratio*	Silica source	1-ADA**	Temp., °C	Days	Stirring
EDP1	[5]	P	Ludox	SS	160	5	-
EDE2	[2]	E	TMOS	SS	160	21	+\$
EDP3	[5]	E	Ludox	SS	160	5	-
EDP4	[5]	E	TEOS [#]	A	160	10	-
EDP5	[5]	P	TEOS [#]	A	160	10	-
EDP6	[5]	P	Ludox	A	160	5	-
EDP7	[5]	P	TEOS [#]	A	160	5	-
EDP8 ^{##}	[5]	P	Ludox	A	160	5	-
EDE9 ^{##}	[2]	E	TMOS	A	160	25	+\$
EDP10	[5]	P	Ludox	SS	160	5	-

* P: 47ADA:188SiO₂:376EN:52640H₂O, E: 47ADA:100SiO₂:404EN:11240H₂O

** SS: in-house prepared from 1-ADA.HCl and NaOH, A: purchased from Aldrich

[#] TEOS was hydrolyzed for 24 hours

^{##} 0.1% wt. of Sigma-1 seed crystals was added to the synthesis solution

^{\$} Autoclave Engineers rotating autoclave was used in case of EDE2 sample and a magnet stirrer was used in case of EDE9 sample

3.3 Sigma-1 zeolite crystals synthesis

Hydrothermal syntheses of Sigma-1 crystals were performed according to the method described by Stewart, examples 1 and 2 [6] (Table 2). Synthesis solutions were prepared in teflon beakers using 1-ADA (97%, Aldrich) or 1-ADA.HCl (>99%, Fluka), silica sol (Ludox, 30% wt., Aldrich), sodium aluminate (50-56% Al, 40-45% Na, Riedel-de Haën) and NaOH (>99%, Merck).

To prepare the synthesis solution, the following operations were carried out: in the first Teflon beaker 1-ADA was dispersed in silica sol and then water was added. Another Teflon beaker was charged with water, sodium aluminate and aqueous solution of sodium hydroxide. The mixtures were then merged and the resulting mixture was stirred for 30 minutes before charging to autoclave. The autoclave was heated to 180⁰C in an oil bath and maintained at this temperature under autogenous pressure for ca 6 days under stirring.

When the synthesis was completed the autoclave was cooled down to room temperature and discharged. The sediment formed in the autoclave was filtered and washed thoroughly with 2 liters of deionised water. The resulting solid was dried in the oven at 50⁰C. The resulting solid was calcined in air for 48 hours at 500⁰C.

The obtained samples were characterized by FT-IR and FT-Raman spectroscopy, SEM, XRD and BET.

Table 2. Sigma-1 zeolite syntheses.

Synthesis	Method	Ratio*	Silica source	Template	Temp., ⁰ C	Hours	Stirring
ESP1	[6], ex. 1	1	Ludox	1-ADA	180	139	+
ESP2	[6], ex. 2	2	Ludox	1-ADA.HCl	180	144	+
ESP3	[6], ex. 1	3	Ludox	1-ADA	180	139	+

* 1: 3Na₂O:20ADA:Al₂O₃:60SiO₂:2400H₂O, 2: 13Na₂O:20ADA.HCl:Al₂O₃:60SiO₂:2400H₂O, 3: 3Na₂O:20ADA:Al₂O₃:60SiO₂:1680H₂O

3.4 Characterization of zeolites

The XRD patterns were recorded on a Siemens D500 diffractometer using Cu-K α radiation. Data were collected between 5 and 35 2-theta degrees, in steps of 0.020 degrees and step time of 6 s. Samples for analysis were prepared in two different ways. When larger amounts were obtained, the powder was grounded, placed into a holder and pressed with a glass plate to make the surface smooth. Measurements were performed while rotating the sample at 30 rpm. When only small sample amounts were available, the solid was dispersed in acetone or methanol and then dripped onto a silicon wafer and the XRD pattern was recorded without rotation.

SEM images were recorded with a Philips XL 30 Scanning Electron Microscope equipped with a LaB₆ filament. The samples were coated with a thin layer of gold to provide conductivity.

Infrared spectra were recorded using a Bruker IFS66v/S spectrometer equipped with a nitrogen cooled mercury cadmium telluride (MCT) detector and a DRIFT attachment. The sample was mixed with KBr in 1:9 ratio. Raman spectra were recorded using a Perkin Elmer NIR FT-Raman 1700X spectrometer equipped with a near-infrared Nd:YAG laser operating at 1064 nm, and a InGaAs detector.

The sorption behaviour was tested by measuring nitrogen adsorption isotherms volumetrically at liquid nitrogen temperature (-196°C, used in order to increase adsorption) on the calcined powder samples. The setup used was a Micromeritics ASAP 2010. The procedure comprised degassing of the sample in vacuum (5 μ m mercury) at 400 or 450°C, dead volume evaluation with helium, adsorption and desorption measurement with nitrogen. Specific surface area was calculated using the BET equation. Pore size distribution was estimated using BJH desorption curve. Microporosity was estimated with the t-plot method.

4 RESULTS AND DISCUSSION

4.1 1-ADA preparation

The white powder obtained in the preparation of 1-aminadamantane described above was characterized by FT-Raman in order to confirm that 1-adamantanamine was obtained. The Raman spectrum of the sample is shown in Figure 4.

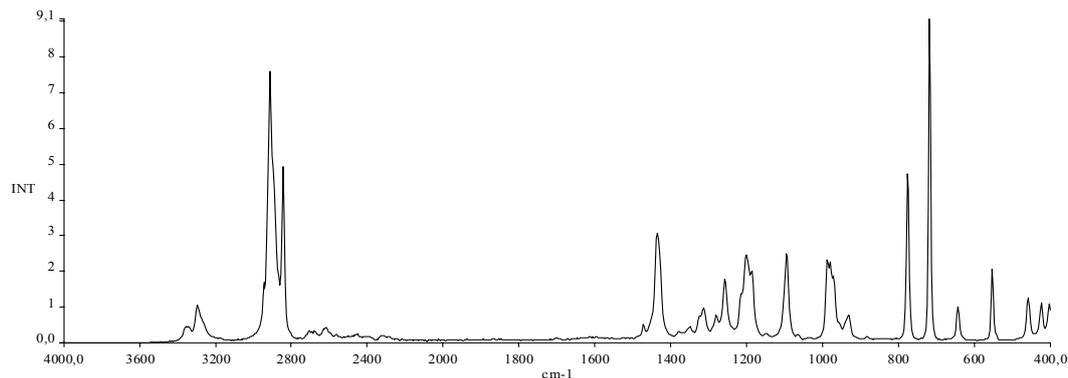


Figure 4. FT-Raman spectrum of the prepared 1-adamantanamine.

The spectrum obtained was compared to the reference available from the web-page of the supplier [19]. The spectra were very similar so the conclusion was made that the prepared powder was 1-adamantanamine.

4.2 Preparation of DD3R clathrasil crystals

Identification of the samples was carried out using X-ray diffractometry. The reference pattern of DD3R is represented in Figure 5 [33].

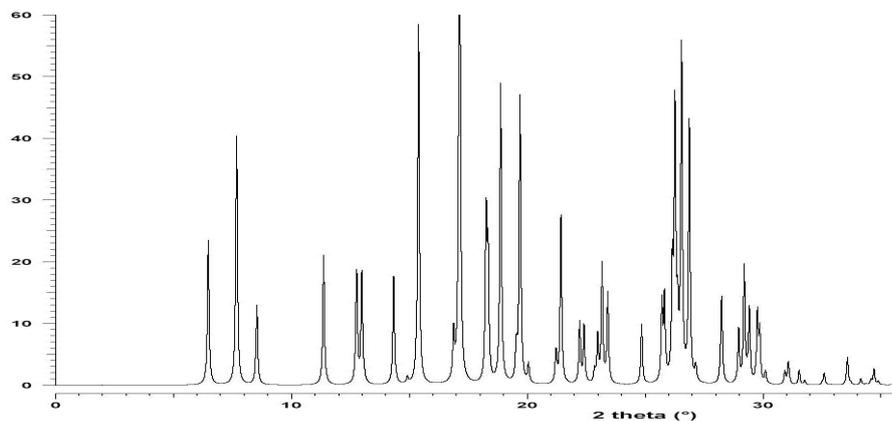


Figure 5. XRD pattern of DD3R clathrasil [33].

Samples EDP1 and EDP3 were prepared according to the method described by K. Nakayama et al. [5], Comparative Example 4. This procedure was developed for preparation of DD3R membranes using a seeding method. But in Comparative Example 4 the authors claim to have got DD3R crystals (but not any membrane) without seed crystals. In our case, the samples obtained were analyzed by XRD before and after the calcination at 700⁰C for 5 hours [2]. The XRD patterns are shown in Figures 6 and 7.

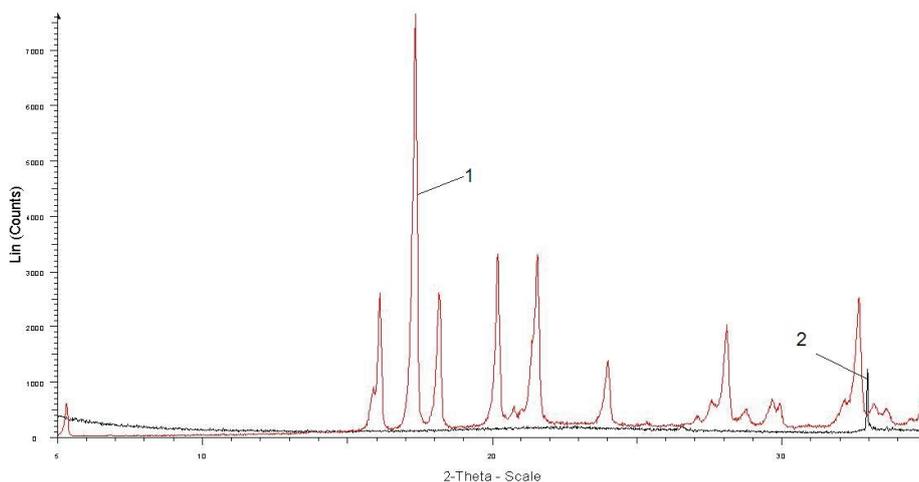


Figure 6. XRD pattern of EDP1 as-synthesized (1) and after calcination (2).

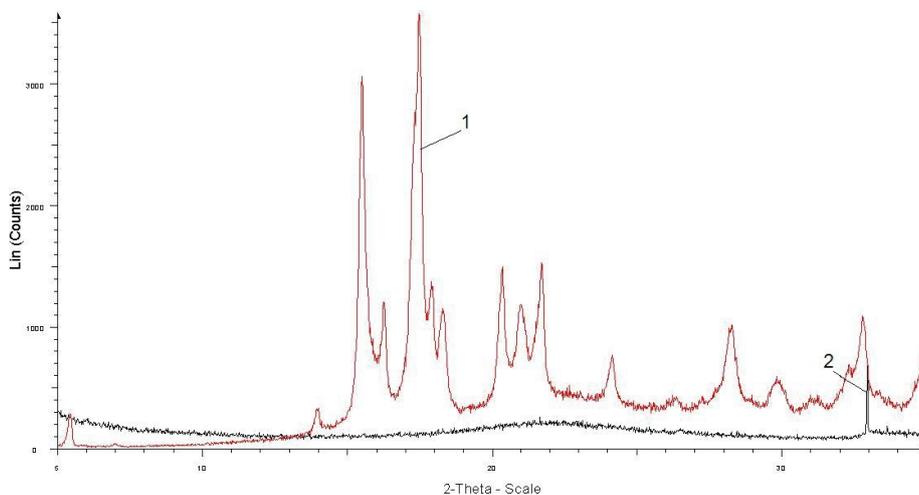


Figure 7. XRD pattern of EDP3 as-synthesized (1) and after calcination (2).

From the figures it can be seen that the materials obtained are not DD3R clathrasil because the patterns do not reveal characteristic reflections of DD3R clathrasil as shown in Figure 5. Both samples have crystalline structure with a small degree of amorphous material (more in case of EDP3). The peak at ca 5.5 2-theta degrees suggests that the samples have large values of interplanar spacing and thus large unit cell dimensions. This feature is common for zeolite materials, which usually show several reflections in the area 5-10 2-theta degrees. After calcination, the amount of

samples substantially decreased and the XRD patterns of the calcined material reveal amorphous structure. The only peak at 33 2-theta degrees originated from the silicon wafer which was used as support to the sample. This observation may suggest that the samples contained large amount of organic material, probably the template molecule, which became decomposed during calcination or the high calcination temperature might have caused the destruction of the crystal lattice. The compounds obtained could not be identified but several reflections in their XRD patterns are similar to those of 1-ADA used in the syntheses.

An attempt was made to repeat synthesis EDP1 (synthesis labelled as EDP10) using the same 1-ADA prepared from 1-ADA.HCl and NaOH [2], the same material was not obtained. Instead a slightly turbid solution with a small amount of amorphous substance was obtained. The possible reason for that is the change in the structure of the prepared 1-ADA. Through carrying out XRD it was observed that 1-ADA had changed its crystalline structure after being kept in a closed glass beaker for ca 3 months. The XRD patterns are represented in Figure 8.

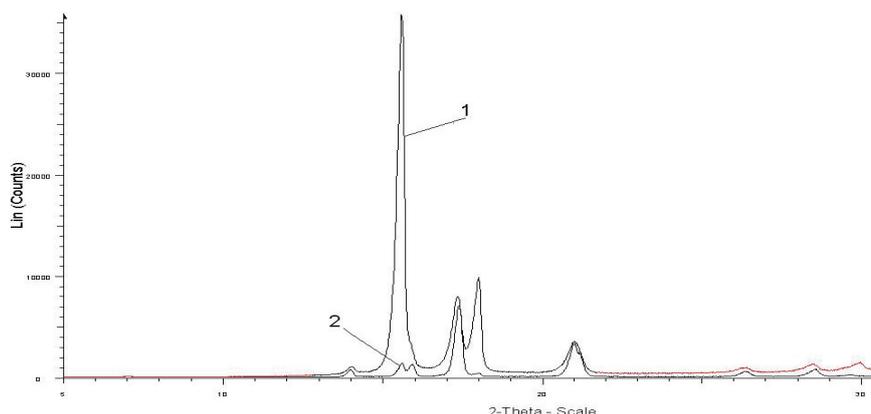


Figure 8. XRD patterns of 1-adamantanamine as-synthesized (1) and aged (2).

Change in the structure of 1-adamantanamine could not be explained.

The EDP1 synthesis was repeated also using 1-ADA purchased from Aldrich (97%) and varying the silica source (see Table 1, samples EDP4-EDP7). None of the syntheses led to the formation of DD3R crystals. Small amounts of colloidal substances were obtained instead (XRD patterns to be found in Appendix 1). Absence of seed crystals might be the possible reason.

Hence it was decided to repeat synthesis EDP1 using 0.1 wt.% Sigma-1 zeolite seed crystals (synthesis of Sigma-1 to be discussed below). No DD3R crystals were obtained in this case either.

Two syntheses were performed in accordance with the method described by den Exter et al. [2]. The main difficulties of this method are that it requires the use of a stirred autoclave and long synthesis time (25 days).

Synthesis EDE2 was carried out using a stirred stainless steel autoclave (Autoclave Engineers) at 150 rpm. The sample obtained was mostly of green colour and possibly contained some metal cations (e.g. chromium, iron), which might have originated from corrosive interaction of the synthesis solution with the stirring mechanism. The XRD pattern of EDE2 is shown in Figure 9.

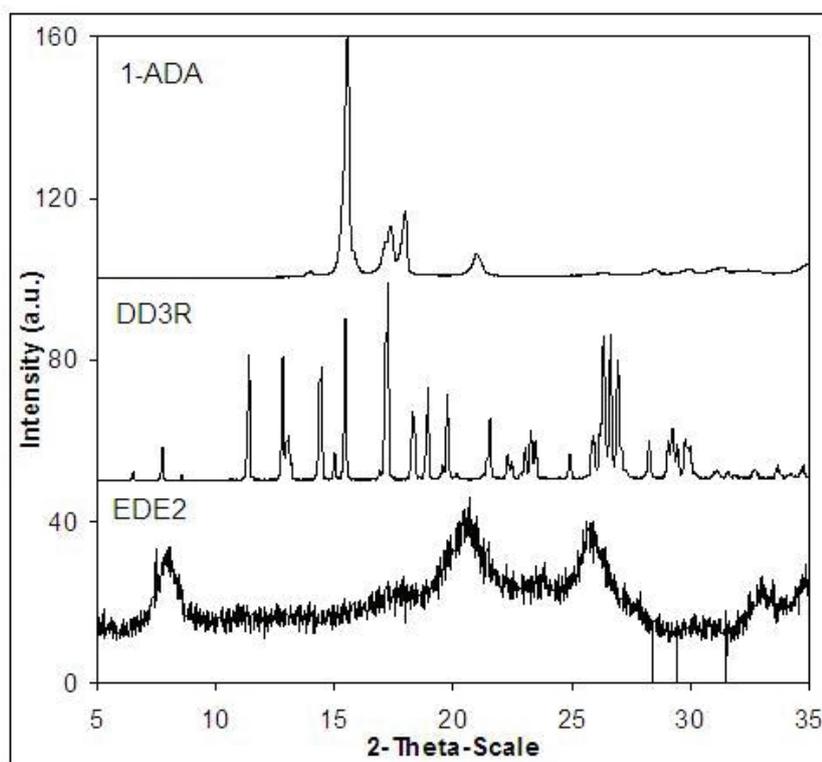


Figure 9. XRD patterns of EDE2, DD3R and 1-adamantanamine.

Considering the XRD pattern it can be concluded that the material is mostly amorphous with some small unidentified crystals present. The reflection at 8 2-theta degrees suggests that it could be some zeolite type substance but with very low degree of crystallinity. The powder does not seem to contain crystals of the template molecule because the most intensive peak of the template is not present in the pattern of EDE2. It might be possible that the crystallization process was in its initial stage when the autoclave was discharged and that is why only small crystals were formed and large amount of amorphous material was obtained. After the calcination performed for 5 hours at 700⁰C the powder changed its color to brick-red and still contained small amount of white particles. The XRD pattern (Appendix A.1) revealed solely amorphous material.

Synthesis EDE2 was repeated (labeled as EDE9) using an ordinary stainless steel autoclave heated in an oil bath and stirred with a magnet stirrer. The synthesis solution was seeded with 0.1 wt.% of Sigma-1 crystals. The obtained sample was calcined in the same way as the sample EDE2. The XRD pattern (Figure 10, a) of the sample is much the same as that of DDR clathrasil (Figure 10, b).

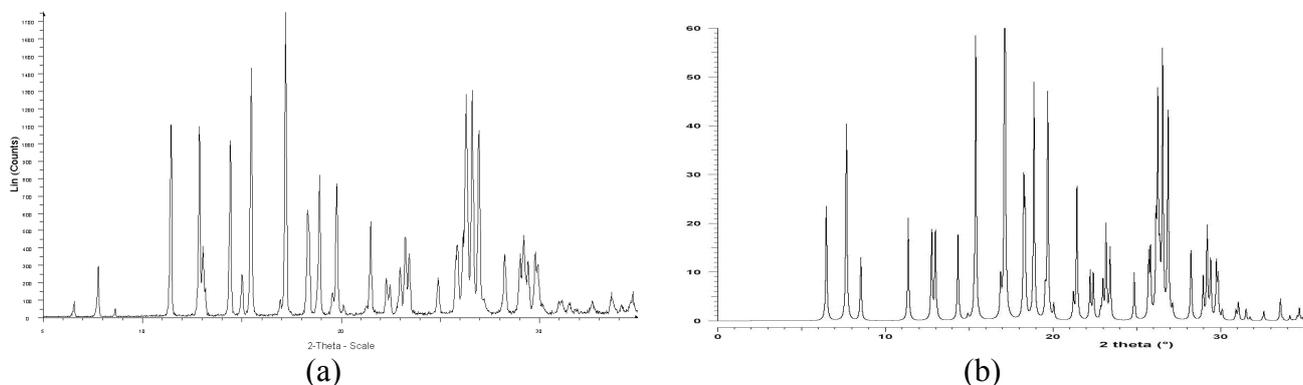


Figure 10. XRD patterns of EDE9 (a) and DDR clathrasil (b) [33].

According to the XRD pattern, the sample has a high degree of crystallinity and contains pure DD3R zeolite material.

The sample used as seed crystals (ESP1, to be discussed below) contained DDR type zeolite Sigma-1, although having a low degree of crystallinity. The DD3R crystals of the sample EDE9 were also obtained in the form of aggregates (Figure 11, a). But in contrast to the seed crystals, DD3R crystals had distinct trigonal shape and the size was between 2 and 10 μm (Figure 11, b). Crystals of approximately the same size and shape have previously been reported [2, 4].

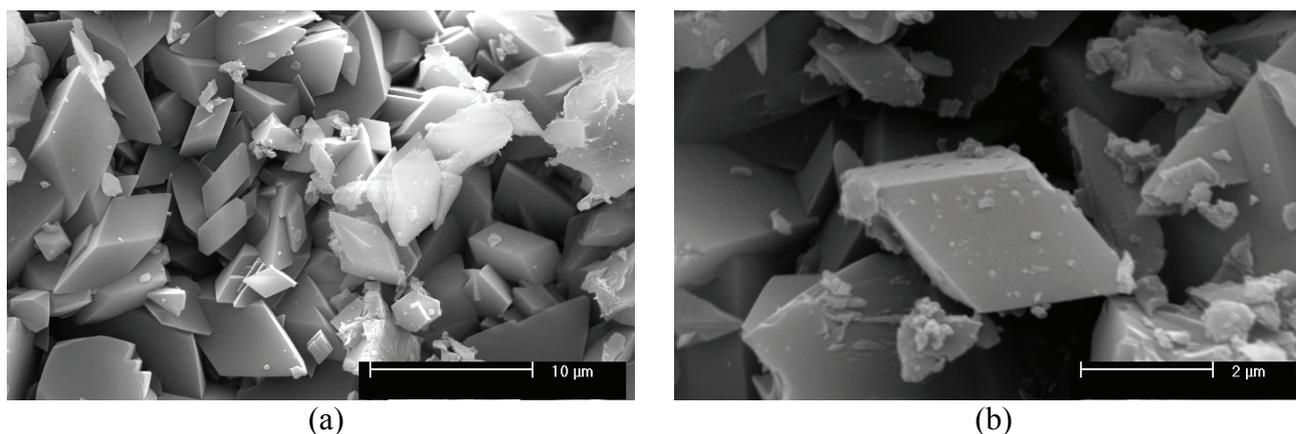


Figure 11. SEM images of EDE9.

The results of nitrogen adsorption/desorption measurements of EDE9 are represented in Table 3. Den Exter [34] reported BET surface area of DD3R 382 m^2/g and total pore volume 0.14 cm^3/g measured with nitrogen at 77 K. The calculated microporosity of DD3R is 0.175 cm^3/g assuming

that the 19-hedrons are the only cages accessible to sorbates [21]. Himeno et al. [4] reported the same values to be 304 m²/g and 0.153 cm³/g respectively. In our case the values mentioned above are lower (Table 3) that might be ascribed to presence of amorphous material or to insufficient calcination.

Table 3. Sorption measurement results of EDE9.

Sample	EDE9
Degassing temperature, °C	400
BET surface area, m ² /g	293.5
BJH desorption cumulative pore surface area (1.7-300 nm), m ² /g	30.8
Micropore area, m ² /g	243.7
External surface area, m ² /g	49.8
BJH desorption cumulative pore volume (1.7-300 nm), cm ³ /g	0.017
Micropore volume, cm ³ /g	0.11
Average pore size, nm	1.87

According to sorption tests, EDE9 is characterized by Langmuir type adsorption isotherm (Type 1) common for microporos zeolite materials (Figure 12). The amount of gas adsorbed increases rapidly up to a limiting value when the micropores are saturated, and then stays almost constant.

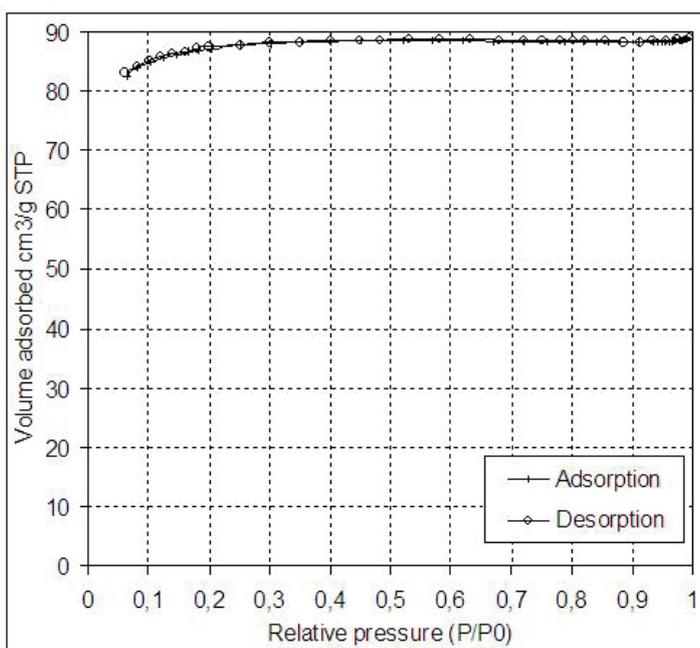


Figure 12. Sorption isotherm of EDE9 (degassed at 400°C).

In Figure 13 pore size distribution of EDE9 is shown. The results suggest that the material obtained has mainly micropores and some small mesopores that are more likely the voids between single crystals in aggregates.

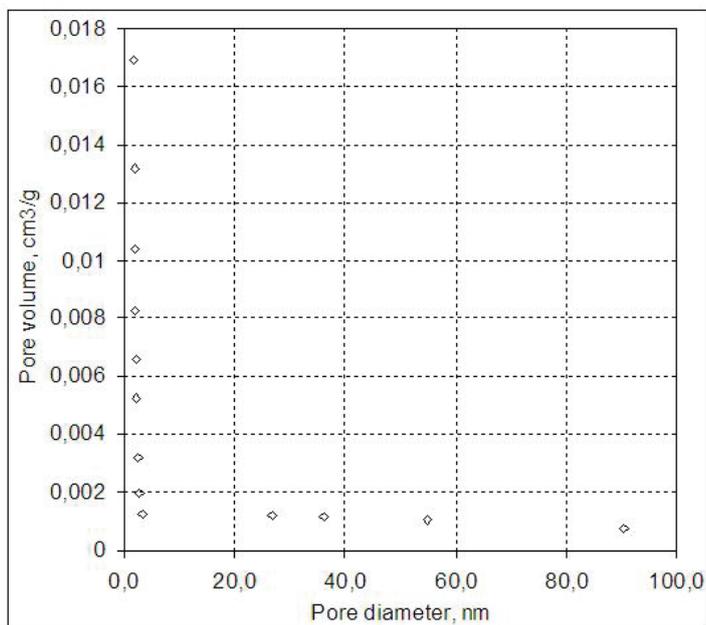


Figure 13. Cumulative pore volume of EDE9 (degassed at 400⁰C).

The results of the syntheses performed are summarized in Table 4.

Table 4. DD3R clathrasil syntheses results.

Synthesis	Description of the as-synthesized sample	Approximate composition	Description of the sample after calcination
EDP1 EDP3	White-yellowish crystalline powder with significant amount of amorphous material	Unidentified silicate with traces of 1-ADA	White amorphous material, noticeably decreased in amount
EDE2	Green powder with very small amount of white particles, mostly amorphous phase with some crystals of small size	Unidentified material probably containing some metal cations	Brick-red powder with very small amount of white particles, amorphous phase
EDP4- EDP8 EDP10	Very small amount of colloidal material with traces of white powder, reveals amorphous structure	Unidentified material	No calcinations performed
EDE9	White crystalline powder	DD3R clathrasil	White crystalline powder

4.3 Preparation of Sigma-1 crystals

Identification of the samples was carried out using X-ray diffractometry. XRD patterns of the samples were compared to the reference pattern of Sigma-1 (Figure 14, b) [6].

The sample ESP1 was prepared according to Example 1 [6] using pure 1-ADA as a template molecule. The XRD pattern of the sample is shown in Figure 14, a.

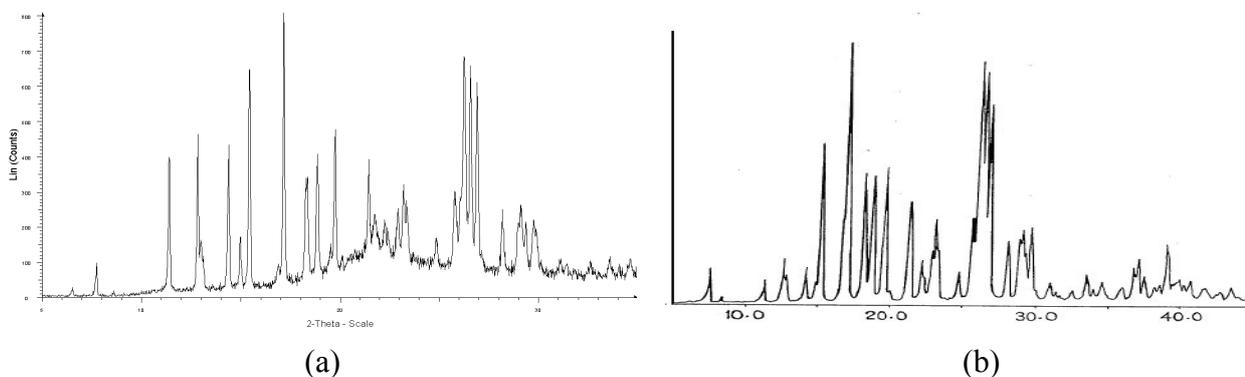


Figure 14. XRD pattern of ESP1 calcined.

The sample ESP1 appears to have almost the same reflections as those corresponding to DDR type zeolite. The pattern of ESP1 sample has a large background suggesting that there is quite a lot of amorphous material present. This fact is confirmed by the SEM image (Figure 15, a), which reveals small (ca 100 nm) not well-defined crystals against the amorphous background. Crystals of the same size and shape were obtained by Tomita et al. in [1]. In Figure 15 (b) four types of particles can be seen: aggregates of small crystals (1), smaller round tablets (2) and bigger tablets (3), needles (4). Types (2) and (3) are similar to Sigma-1 particles obtained by Stewart et al. in [21]. Large rounded particles (3) in Figure 15 (b) are similar to the ZSM-58 crystals reported by Olson et al. [22].

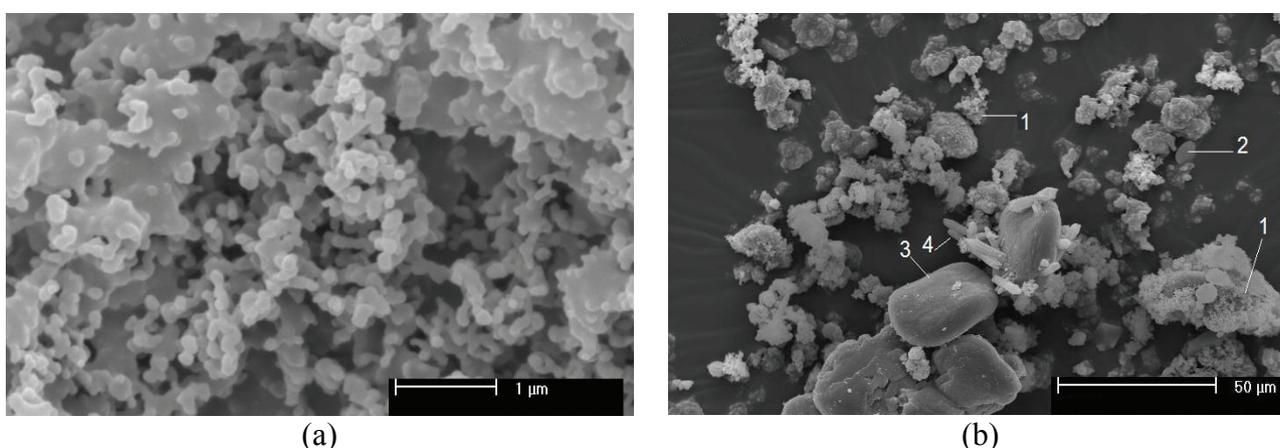


Figure 15. SEM images of ESP1.

Though different template molecules are used in Sigma-1 and ZSM-58 synthesis, ZSM-58 has the same crystal structure as Sigma-1 according to the X-ray diffraction. Thus, it might be possible that

crystals of the same morphology as those of ZSM-58 zeolite could be obtained in Sigma-1 synthesis.

The difference in the morphology of the crystals obtained might be explained by the fact that the concentration of the synthesis solution varies along the height of the autoclave owing to insufficient stirring. When the autoclave was discharged, fine white powder was found on the bottom where stirring was most intense and large yellowish aggregates were found in the pellet formed on top of the solution.

In the synthesis ESP2, the hydrochloric form of 1-ADA was used and thus more NaOH was added to the synthesis mixture in order to neutralize H^+ and Cl^- ions. The XRD pattern of ESP2 is represented in Figure 16.

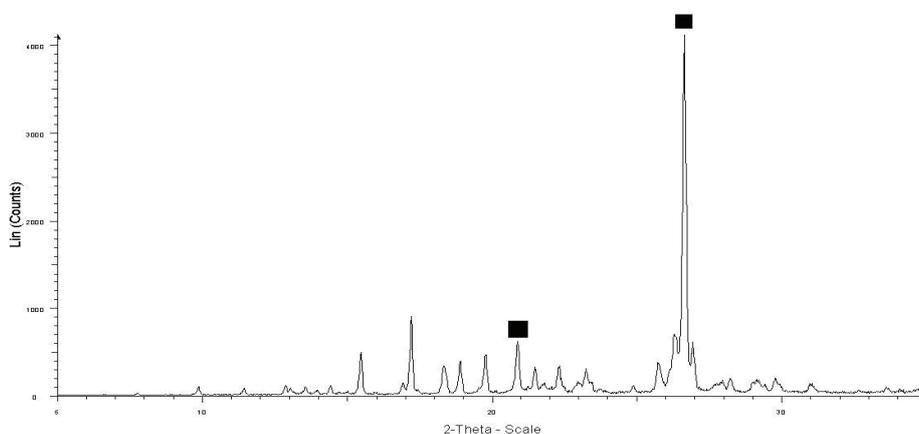


Figure 16. XRD pattern of ESP2 calcined, peaks of synthetic quartz are marked with (■).

The pattern has all the peaks corresponding to DD3R zeolite but also some extra peaks including those of alpha-quartz crystals. Mordenite and crystalline silicas such as α -quartz and α -cristobalite are known to be formed at high free OH^-/SiO_2 ratios. At intermediate ratios ZSM-5 and α -cristobalite are formed [21]. Quartz crystals have the shape as shown in Figure 17.

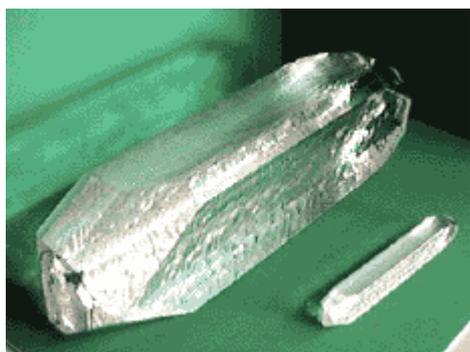


Figure 17. Synthetic quartz crystals [35].

Similar needle-shaped crystals (1) were found in the obtained sample, see Figure 18 (a, b).

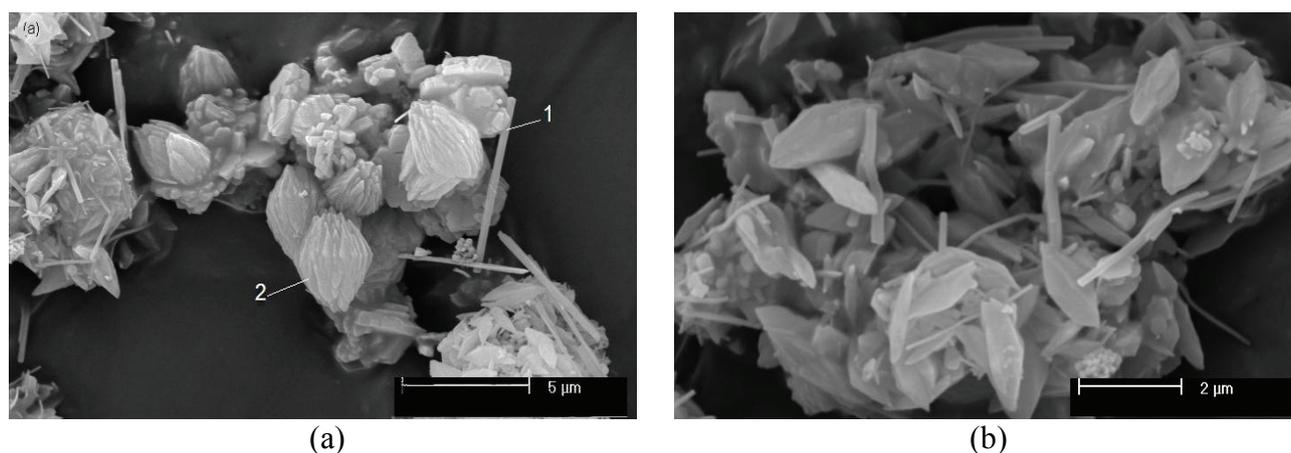


Figure 18. SEM images of ESP2.

In addition, thistle-shaped crystals (2, Figure 18, a) and trigonal DD3R crystals (Figure 18, b) can be found. The thistle-shaped crystals are very similar to the polymorph crystals of DOH and DD3R obtained by den Exter et al. [2]. But in our case the presence of DOH was not confirmed by the XRD pattern.

The diffuse reflectance FT-IR (DRIFT) spectra of the calcined samples (Figure 19) reveal two main absorbance bands in common with other zeolites: the stretch of the Si-O situated near to 1100 cm^{-1} and the deformation of the Si-O situated near 500 cm^{-1} .

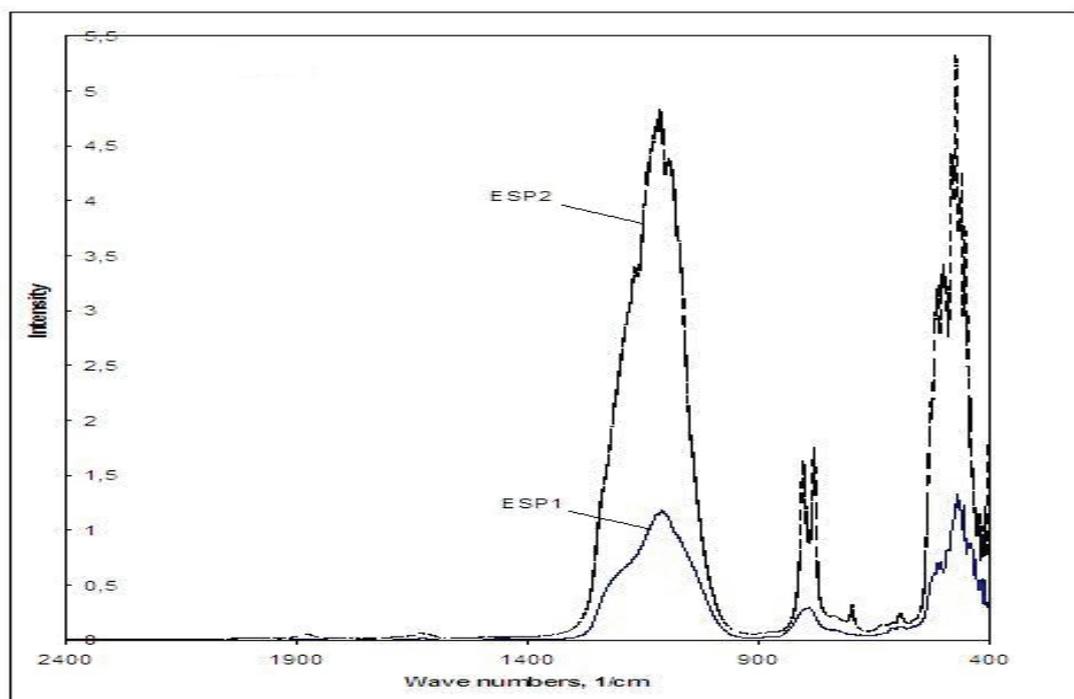


Figure 19. DRIFT spectra of Sigma-1 samples (as Kubelka-Munk).

The spectrum of ESP1 is very similar to the ones described by den Exter et al. and Stewart [2, 6], whereas ESP2 shows some noticeable difference, which might be attributed to quartz co-crystallized.

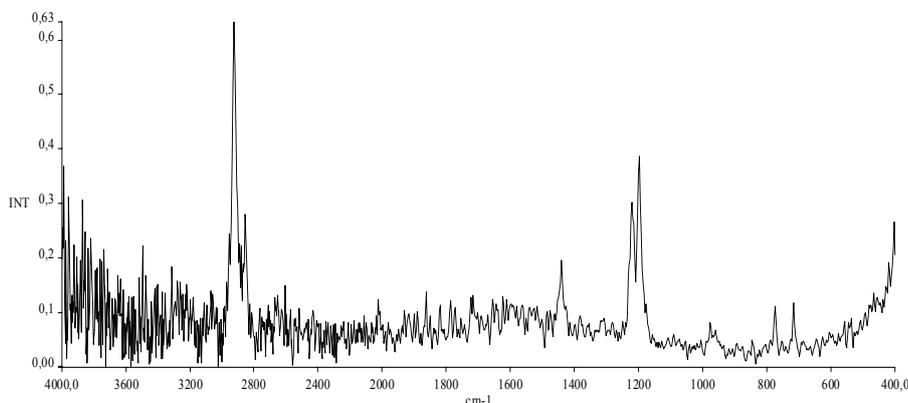


Figure 20. FT-Raman spectrum of ESP1 (as-synthesized).

The bands observed in the FT-Raman spectrum are described in Table 5.

Table 5. Observed bands in the Sigma-1 FT-Raman spectra.

Frequency, cm^{-1}	Type of vibration
1200 [36, 37]	ν_{as} (Si-O)
1463 [38]	$2\delta_{\text{as}}$ (CH_2)
2854 [38]	ν_{s} (CH_2)
2927 [38]	ν_{as} (CH_2)

No reference FT-Raman spectrum was found for any DDR type zeolite. But according to the data available from the literature a conclusion can be made that the materials obtained have the bands ascribed to asymmetrical stretching of Si-O bonds. Besides, the bands corresponding to stretching and bending vibrations of the methylene groups can be seen in the spectra, these are assigned to the template molecule still present in the structure of the as-synthesized material.

The results of the surface area and pore size distribution evaluation of Sigma-1 samples are represented in Table 6. The values of BET surface area and micropore volume are approximately 2 times lower than those reported by den Exter [34] and Himeno et al. [4] that might be ascribed to presence of amorphous material revealed from the XRD pattern. With the increase of degassing temperature the micropore volume increases as well, due to better removal of adsorbed compounds and crystalline water from the structure of the zeolite.

Table 6. Sorption measurement results of Sigma-1 samples.

Sample	ESP1		ESP2	
Degassing temperature, °C	400	450	400	450
BET surface area, m ² /g	140.0	139.5	161.0	163.3
BJH desorption cumulative pore surface area (1.7-300 nm), m ² /g	18.3	14.5	0.58	5.5
Micropore area, m ² /g	116.5	119.4	138.0	140.4
External surface area, m ² /g	23.5	20.0	23.0	22.9
BJH desorption cumulative pore volume (1.7-300 nm), cm ³ /g	0.035	0.026	0.010	0.014
Micropore volume, cm ³ /g	0.054	0.055	0.064	0.065
Average pore size, nm	2.28	2.24	2.36	2.37

According to adsorption tests, Sigma-1 samples are characterized by Langmuir type adsorption isotherm (Type 1) common for microporous zeolite materials (Figure 21).

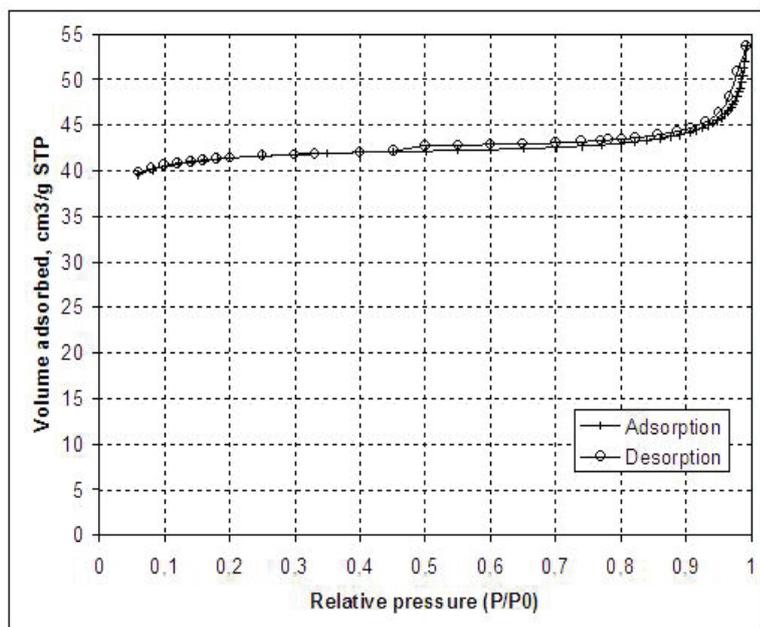


Figure 21. Sorption isotherm of ESP1 (degassed at 450°C).

A small hysteresis loop is the result of capillary condensation of the adsorbate in mesopores between the crystals. In Figure 22, the pore size distribution of Sigma-1 is shown.

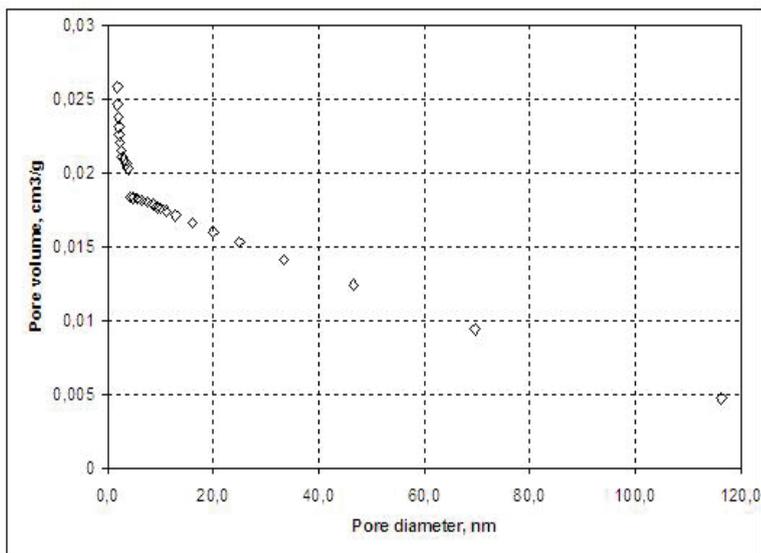


Figure 22. Cumulative pore volume of ESP1 (degassed at 450°C).

The results suggest that the material obtained has a lot of micropores and some meso- and macropores that are actually the voids between crystals.

In the synthesis of ESP3, an attempt was taken to prepare smaller crystals of Sigma-1. For this purpose the amount of water in synthesis gel was reduced by 30% thus increasing the total concentration of the mixture. At higher concentration nucleation is faster that leads to formation of smaller crystals [3].

The synthesis gel obtained was very viscous and hard to stir with a magnet stirrer even at the highest rotation speed. The XRD pattern of the sample is presented in Figure 23.

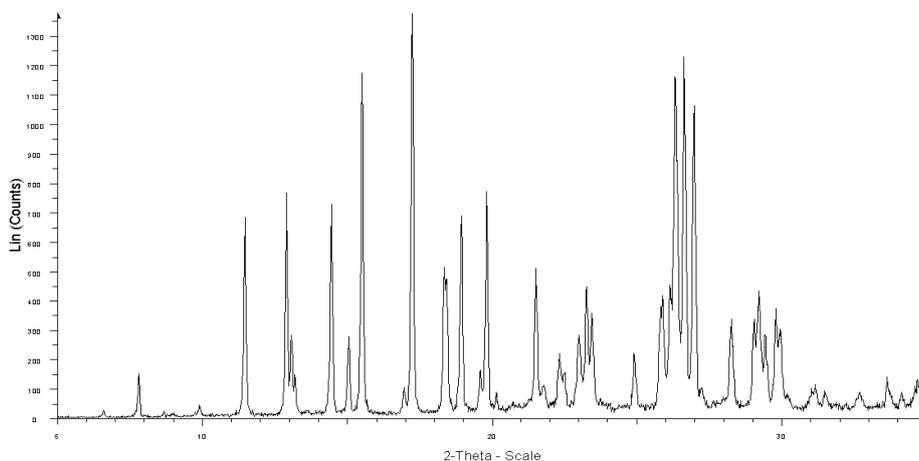


Figure 23. XRD pattern of ESP3 calcined.

The XRD pattern confirms that the obtained material is Sigma-1 zeolite with some amount of amorphous material which might originate from insufficient stirring of the synthesis gel during the synthesis in combination with short synthesis time.

Figure 24 shows SEM images of sample ESP3. The particles formed are uniform in size (ca 15-20 μm) (Fig. 24, a) and represent aggregates of trigonal DD3R type zeolite crystals of the size around 3-4 μm (Fig. 24, b). The formation of aggregates might have been caused by insufficient stirring.

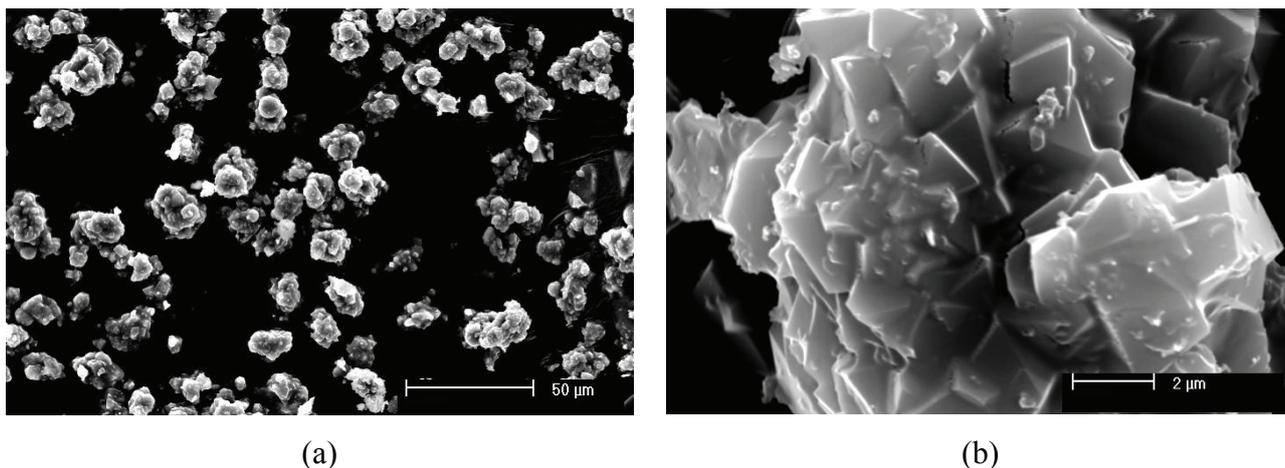


Figure 24. SEM images of ESP3.

The results of the Sigma-1 syntheses performed are summarized in Table 7.

Table 7. Sigma-1 zeolite syntheses results

synthesis	Description of the as-synthesized sample	Approximate composition	Crystal shape and size
ESP1	White fine crystalline powder with big yellowish aggregates	Sigma-1	Small spherical not well-defined 100 nm, needle-shaped 15 μm , tablets 5-10 μm and 20-25 μm .
ESP2		Sigma-1, synth. quartz	Trigonal 2 μm , thistle-shaped 4 μm , needle-shaped >5 μm
ESP3		Sigma-1	Trigonal not well-defined 3-4 μm

5 CONCLUSIONS

DD3R clathrasil and Sigma-1 zeolite crystals were successfully synthesized in amounts enough to facilitate characterization by analytical techniques such as XRD, SEM, BET, FT-IR and FT-Raman spectroscopy.

The method suggested by den Exter et al. appeared to be the only appropriate technique for DD3R clathrasil crystals synthesis. The presence of seed crystals facilitated the crystallization process.

The method of DD3R preparation claimed by K. Nakayama et al. was considered to be not suitable for DD3R crystals synthesis since the results reported by the authors could not be reproduced.

The procedure of Sigma-1 crystals synthesis described by A. Stewart was found to be simple and although the sample obtained was partially amorphous, it was of sufficient quality to be used as seed crystals in DD3R synthesis. It was noticed that proper stirring was required in order to get uniformly sized and shaped crystals.

The results of X-ray diffraction, FT-IR spectroscopy and scanning electron microscopy were in close agreement with those reported previously for DD3R clathrasil and Sigma-1 zeolite. However, the values of surface area and microporosity were found to be lower compared to those available from the literature. This was ascribed to a somewhat low degree of crystallinity of the samples obtained.

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APPENDIX A.1 XRD patterns of the samples.

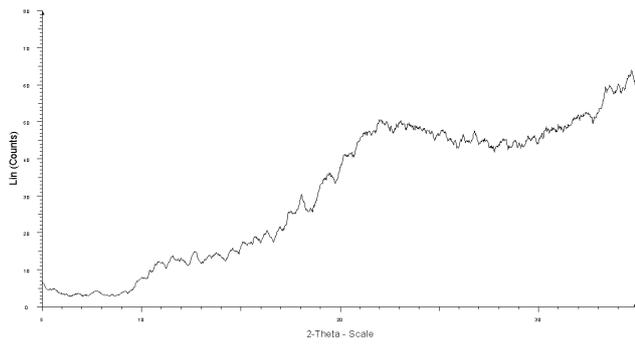


Figure 25. XRD pattern of EDE2 calcined.

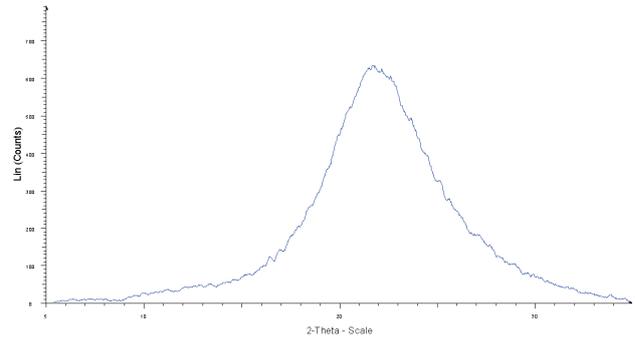


Figure 26. XRD pattern of EDP4.

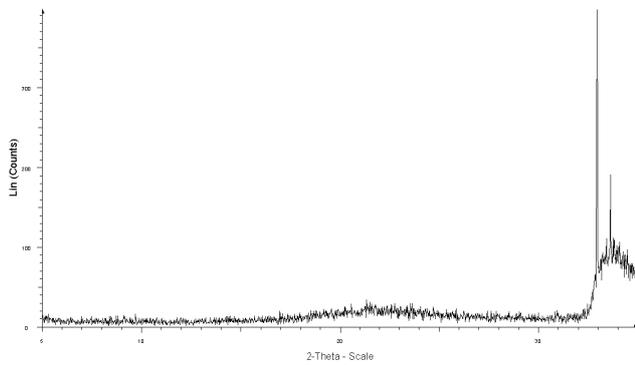


Figure 27. XRD pattern of EDP5.

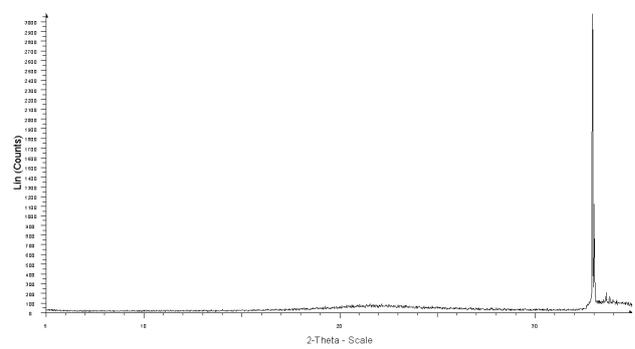


Figure 27. XRD pattern of EDP6.

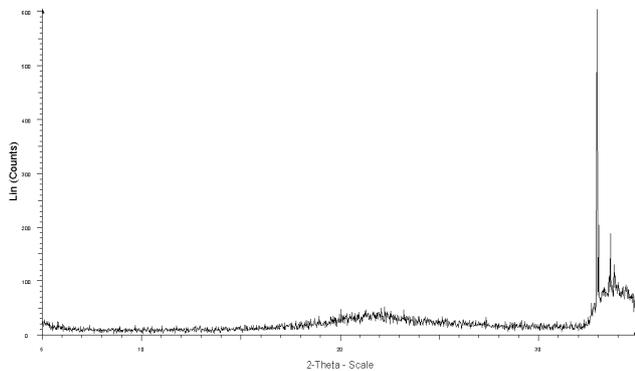


Figure 29. XRD pattern of EDP7.

APPENDIX A.2 *FT-IR and FT-Raman spectra of the samples.*

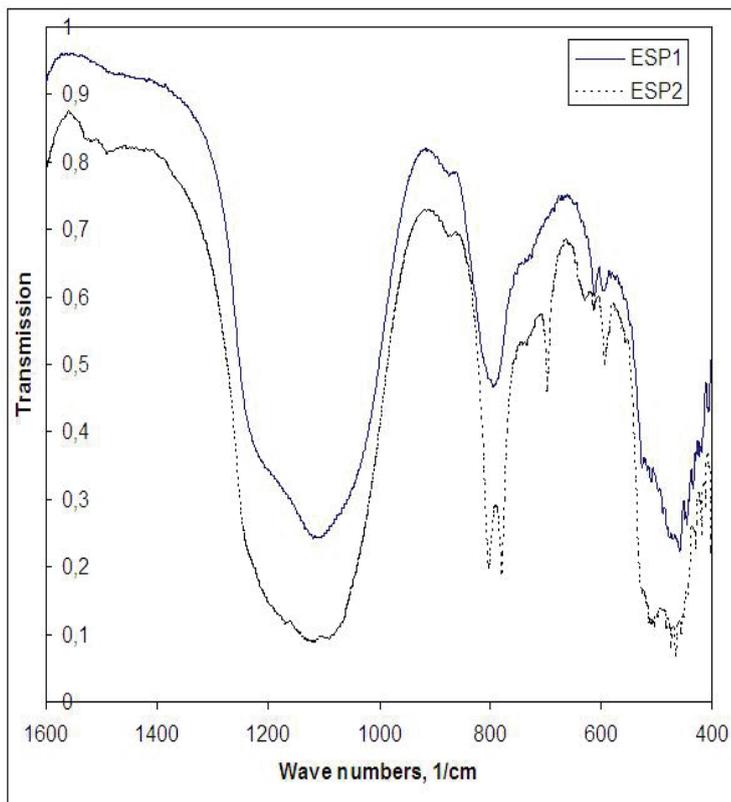


Figure 30. FT-IR spectra of ESP1 and ESP2.

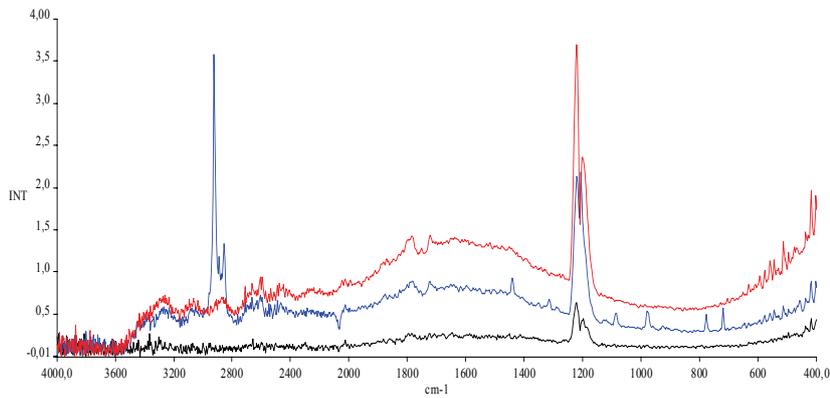


Figure 31. FT Raman spectra for EDP1 calcined, EDP3 calcined, EDP4 (from bottom to top).