Preparation of Ultradispersed Crystallites of Modified Natural Clinoptilolite with the Use of Ultrasound and Its Application as a Catalyst in the Synthesis of Methyl Salicylate

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Abstract: The ultradispersed crystallites (300 – 325 nm) of the acid modified natural clinoptilolite (CL, $\nu(SiO_2)/\nu(Al_2O_3) = 8.9$) from Dzegvi (Georgia) deposit with the use of simplest method – of the indirect effect of ultrasound – were prepared. Under the influence of ultrasound the happening changes of structure and the sizes of clinoptilolite particles are shown, by the XRD, FTIR spectroscopy and by means of laser particle size analyzer, respectively. Catalytic activities of the initial acid form of the clinoptilolite (H–CL, $\nu(SiO_2)/\nu(Al_2O_3) = 23.3$) and its form processed by ultrasound (H–CL (UlS)) in reaction of esterification of salicylic acid by methanol into methyl salicylate were compared. The indirect irradiation with ultrasound of acid form of clinoptilolite has led to sharp improve its catalytic properties in the formation of methyl salicylate. The best catalytic performance is achieved with ultrasound treated catalyst. The conversion of the salicylic acid and the selectivity to methyl salicylate on H–CL (UlS) were very high, 90 and 95%, respectively, at 120°C.

Keywords: Ultrasound, Ultradisperse Clinoptilolite, Esterification, Methyl Salicylate

1. Introduction

Natural and synthetic zeolites are microporous materials. Various methods for the preparation of their nanocrystals with sizes of 5 – 500 nm were currently developed, which are discussed in the latest review papers [1 – 5]. It is known that in nanosized systems including the zeolite nanocrystals the ratio of external to internal numbers of atoms or molecules increases sharply by decreasing the particles sizes [6 – 7]; accordingly, nanosized zeolites have large external surface, a large number of active sites in the outer surface of the crystals, and thus greater activity in contrast to micrometric-sized zeolites; besides micropores the zeolite nanocrystals also have structural mesopores, which are "transport arteries" and this is especially important in the conversion of large molecules [1 – 3, 8].

All this determine their specific catalytic, adsorption, ion-exchange properties and their applications as chemical sensors [2, 8], in the pharmaceutical industry [2], food, for preparation optical quality films [9 – 10] and membranes [11].

Unlike hydrothermal methods of synthesis of nanosized zeolites, sonochemical synthesis by ultrasonic irradiation (20 kHz – 10 Mhz) is a new, unconventional method and it possesses many advantages [12, 13]. Essentially the influence of ultrasound during synthesis of zeolites was investigated. Moreover, improvement of alkylation catalytic activity of the micro-mesoporous zeolite Y synthesized by ultrasonic / microwave synergistic influence is shown [14]. Direct mechanical influence of ultrasound on zeolite H–Mordenite and H–Beta for a long time leads to an increase in the dimension of the elementary cell of zeolites, reduction their particle size, the

decrease pore opening and formation structural defects [15]. Dispersing influence of the ultrasound irradiation on the particles is caused by cavitation (the formation, growth an implosive of collapse bubbles in a liquid [13]).

Preparing, researching and application of an acid form of natural zeolite clinoptilolite with ultradispersed particles (H–CL (UlS)) as a catalyst for preparation of methyl salicylate (MS) was the purpose of the presented research.

MS is an important ester of salicylic acid. It is widely used in medicine, pharmaceuticals, technique, cosmetic and perfumes, in chemistry as chemical intermediate.

MS is obtained from natural resources with steam distillation of oils of some plants (Gaulteria procumbes, Betula lenta, Spraea), but oil output is low and mainly MS is produced synthetically [16].

MS is synthesized by esterification reaction of salicylic acid with methanol. Because of the reversibility of this reaction it is carried out in the presence of homogeneous or heterogeneous acid catalysts such as H_2SO_4, HCl, $AlCl_3$, clays, zeolites H–Beta, H–ZSM–5, HY [17], mesoporous materials, sulphated metal oxides [18], heteropolyacids, modified ion-exchange resins [19], and also of ionic liquids which are the most "green" catalysts; but their high cost prevents their use in industry [20].

In the presence of heterogeneous catalysts known to date, yields of MS are relatively low. Therefore in industry the above stated mineral acids and, generally sulphuric acid are applied as the catalyst for synthesis of MS. These systems are environmentally harmful and there is a problem to replace them with more harmless and highly active catalysts.

In scientific literature there is also a research on efficiency of combined use of H_2SO_4 and microwave radiation [21]. It considerably reduces reaction time in comparison with one sulfuric acid from 4 – 5 h to 10 – 40 min that prevents the equipment from corrosion and saves energy.

We got the sample H–CL (UlS) by the indirect effect on acid form of natural zeolite clinoptilolite H–CL through a water of the water bath of ultrasonic cleaner (DSA100–SK) with frequency and power, 40 kHz and 100 W, respectively.

The properties of the parent acid form of clinoptilolite (H–CL) and H–CL (UlS) processed by ultrasound were characterized by the methods XRD, FTIR-spectroscopy, by means of laser particle size analyzer and by the static method for investigation catalytic reactions.
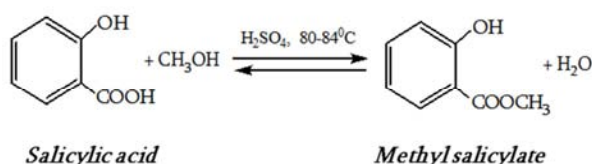

Figure 1. Reaction for synthesis of methyl salicylate.

Sharp increase in catalytic activity in methyl salicylate synthesis by reaction of esterification of salicylic acid with methanol (Figure 1) on the catalyst processed by ultrasound and containing ultradispersed particles is shown.

2. Experimental

2.1. Chemicals and Materials

In the esterification reaction the following chemicals were used: salicylic acid (99.65 %, "Stanchem", Poland) and methanol LC–MS ($\geq$ 99.9 %, LC–MS Ultra Chromasolv, Sigma–Aldrich). As catalysts solid acids were used: H-form of heulandites family natural zeolite – clinoptilolite, H–CL, and treated with ultrasound its form H–CL (UlS).

2.2. Preparation of Catalysts

The catalysts have been prepared from the museum sample of natural zeolites of Georgia – clinoptilolite-containing rock (CL, $\nu(SiO_2)/\nu(Al_2O_3) = 8.9$) from Dzegvi (Georgia) deposit.

According to previous data the CL contains about 95 % of clinoptilolite, a minor amount of α-quartz and feldspars [22].

Rocks of natural CL (starting form of natural clinoptilolite), was ground in an agate mortar down to a powder finer than 6 μm, washed with the distilled water and dried at 80°C to remove soluble impurities. Then solid acid catalysts H–CL and H–CL (UlS) were prepared according to the following procedures:

Catalyst H–CL. Starting form of natural CL was leached once with 1 M HCl solution (10 ml solution / g zeolite) for 4 h at reflux temperature. Then the suspension was filtered and the precipitate was washed with hot distilled water until a negative reaction for chlorine ions, dried in air at 40°C.

Catalysts H–CL (UlS). 4 g of milled in an agate mortar H–CL sample in the beaker was diluted with distilled water (10 %); the suspension was subjected to ultrasonication in ultrasonic cleaner, in water bath; sample of catalyst H–CL was processed ultrasound sequentially within 0.5, 1,2, 5.5 and 7.5 h. By ultrasonic treatment of a zeolite, an increase in water bath temperature up to 55°C was observed and it was held up to the end of this procedure. Then the suspension was freely evaporated on an air. Immediately, after irradiation the size distribution of particles in the initial and irradiated samples was determined.

Before the catalytic experiences all catalysts were warmed up for 3 h in a flow of a pure air at 300°C.

2.3. Characterization of Catalysts

X-ray fluorescence analysis using energy dispersive X-ray fluorescence spectrometer EDX3600B (Skyray Instrument Ltd., China) the partial chemical composition of catalysts was determined.

X-ray powder diffraction analysis was performed using a diffractometer DRON–4 with Cu–K_α (λ = 0.15406 nm; 40 kV, 16 mA) radiation at room temperature; diffraction patterns were recorded in the range $2\theta = 5 – 50$ ° at a scanning rate of 2° / min. XRD patterns were used to identify the zeolites crystalline phases. By the values of the intensities of the characteristic bands on the diffractograms the relative degree of crystallinity of the studied zeolites was determined [23, 24].

Fourier transform infrared spectroscopy (FTIR) studies of catalysts were conducted on a FTIR spectrometer Varian 660–

IR in the infrared region 2000 – 400 cm^{-1}; band intensities were denominated in transmittance. Samples were prepared with KBr; before registering the spectra of zeolite and KBr powder mixture in a weight ratio of 1/350 were compressed with a hand press.

Particle size determination. After ultrasonic processing the distributions by the size so f crystallites of catalysts H–Cl (UlS) and H–CL on the laser light scattering particle size analyzer (Laser-Particle Sizer Analysette 12–Dyna Sizer, Fritsch) by Cumulants and Pade–Laplace algorithms were determined. Size distribution was expressed in terms of intensity and volume.

2.4. Catalytic Activity, Analysis of Reaction Products

The esterification reaction of salicylic acid with methanol was performed in the liquid phase in a 50 ml three-necked round bottomed glass flask with a reflux condenser, thermometer and a port for periodical sampling of reaction mixture by a capillary; reagents and catalyst were stirred by a magnetic stirrer with heater.

The catalytic reaction of esterification was investigated in static system in the following conditions: the mass of the catalyst was 0.1 – 0.5 g, molar ratios of SA / methanol 1/2 – 1/10, temperature from 40 to 140°C, at atmospheric pressure. The analysis of products of catalytic reactions was carried out by the GC–MS methods (Agilent Technologies, 5890B/5977A, capillary column HP–5ms, Ultra Inert, 30 m × 0.32 mm × 0.25 μm) and UV spectroscopy (Specord UV–VIS, Germany). The reaction mixture consisted essentially of methyl salicylate, of unreacted salicylic acid, and small amounts of phenol and phenyl salicylate.

Monitoring of reaction was carried out by the periodic sampling of reaction mixture and its UV spectroscopic analysis on the content of methyl salicylate $\lambda_{max} = 237.0 - 237.9$ nm [25].

The reaction mixture was dissolved in the diethyl ether; the lower layer in the formed two phases was the catalyst and water, in the upper – an organic part of the reaction product. The latter was separated by decantation and analyzed by GC–MS using standards. Calculations of conversion (*C*) of salicylic acid, and of yield (*Y*) and selectivity (*S*) of methyl salicylate were carried out, respectively, on the following formulas:

$$C = (m_{\text{initial SA}} - m_{\text{remaining SA}}) \times 100 / m_{\text{initial SA}},$$

$$Y = (m_{\text{obtained MS}} / m_{\text{theoretical MS}}) \times 100,$$

$$S = 100 \times Y / C.$$

Here *m* is the mass of a substance.

3. Results and Discussion

3.1. Powder XRD Patterns and FTIR Spectra of Catalysts

From Table 1 it is visible that for the studied derivatives of a natural clinoptilolite H–CL and H–CL (UlS) a molar ratio

$\nu(SiO_2)/\nu(Al_2O_3)$ is very big (23.3), i.e. they represent deeply dealuminated and decationized samples.

Table 1. *Ratio of intensities (I) of the characteristic XRD peaks of the catalysts at 2θ = 9.88, 22.36 and 30.05 ° to the quartz peak intensity at 26.60 ° (I$_0$).*

Catalysts	Natural clinoptilolite, CL	H–CL	H–CL (UlS)
$\nu(SiO_2)/\nu(Al_2O_3)$	8.90	23.30	23.30
$I_{9.88°}/I_0$	0.95	0.78	0.57
$I_{22.36°}/I_0$	2.65	1.44	1.23
$I_{30.05°}/I_0$	1.40	0.47	0.46
$\sum I/I_0$	5.00	2.69	2.26
*AVRC, %	95	51	43

*AVRC – Average value of relative crystallinity

The Figure 2 shows, that powder XRD patterns of all the studied catalysts contain characteristic diffraction lines of the HEU-type zeolite – clinoptilolite at 2θ = 9.88, 22.36 and 30.05 ° [26].
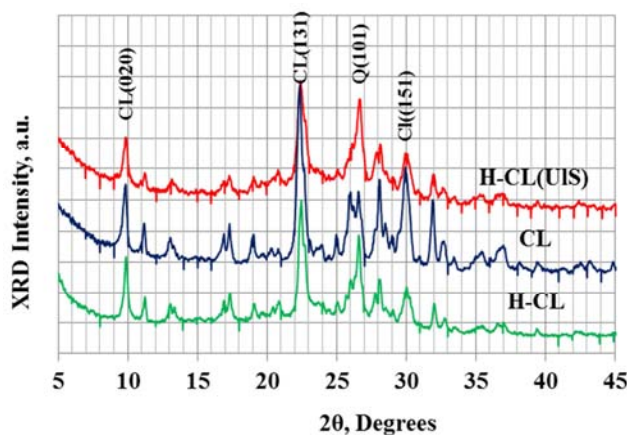

Figure 2. *Powder XRD patterns of catalysts – natural clinoptilolite CL, its acid-treated form H–CL and of sample H–CL (UlS) obtained by ultrasonic irradiation of H–CL for 7.5 h.*

The data in Figure 2 and Table 1 show that intensities of these diffraction peaks are reduced for samples of H–CL and H–CL (UlS) in comparison with the natural clinoptilolite (CL). This decrease was characterized by the ratio of intensities (*I*) of characteristic peaks of a clinoptilolite (2θ = 9.88, 22.36 and 30.05 °), to that for a quartz phase at 2θ = 26.6 ° (*I$_0$*) which was present in clinoptilolite. Reduction of intensity of a sample of H–CL is connected with the known removal of cations and aluminium from a clinoptilolite at its processing by acid [23].

From the Table 1 it is also evident that in the case of catalyst H–CL (UlS) with ultrasonic irradiation during 7.5 h decline in the relative intensity of diffraction peaks (*I/I$_0$*), especially of the diffraction peaks at 9.88 and 22.36 °, corresponds to a decrease in its crystallinity compared to the H–CL by 8 %. The similar phenomena are described earlier with respect to H-Mordenites and H-Beta zeolite, processed by ultrasound [15].

As shown in the Figure 3, FTIR spectra of the catalysts H–CL and H–CL (UlS) are similar, but for catalyst treated ultrasonically the shifting of some bands are observed; in particular, from structure sensitive band at 603.46 and structure insensitive bands at 465.29, 1083.44, respectively, to 607.45 and 462.25, 1079.65 cm^{-1}.
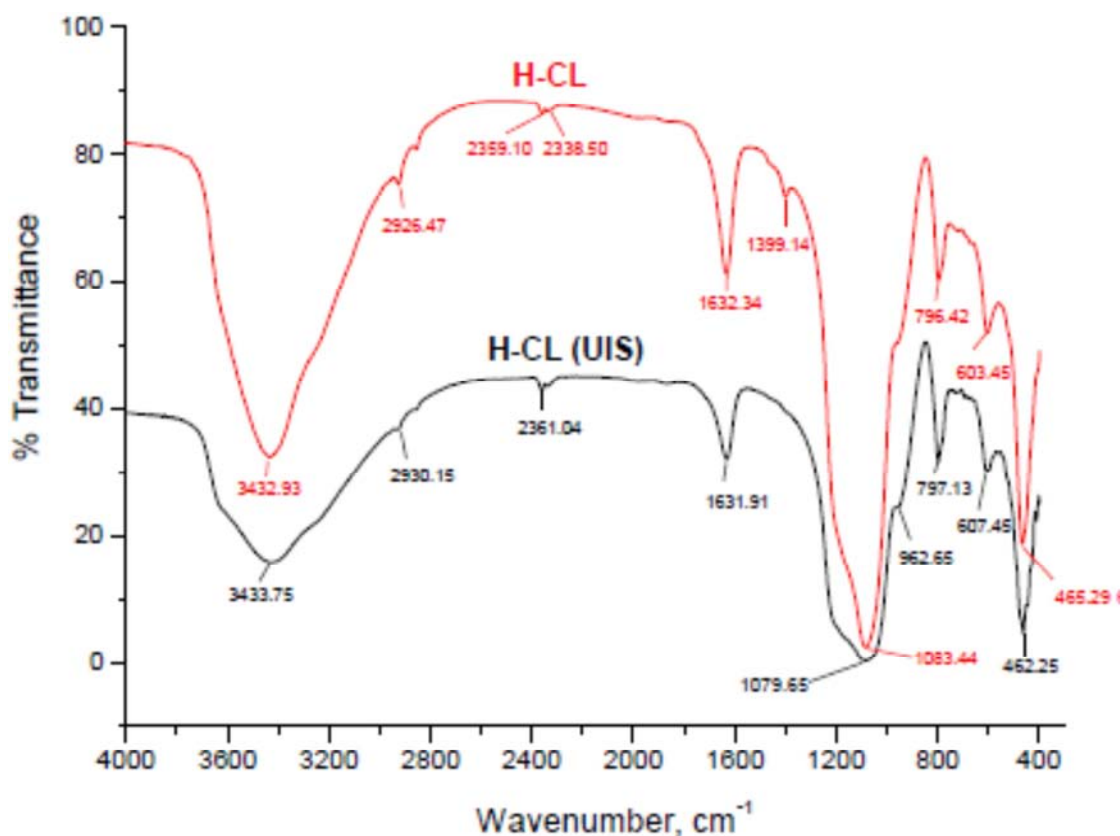
Figure 3. FTIR spectra of the acid form of the natural clinoptilolite (H–CL) and its H–CL (UlS) form processed by ultrasound within 7.5 h.

The band at 465.29 cm^{-1} (bending vibration T–O, T = Al, Si), is characteristic to the pore opening [27]. The shift of strong band at 465.29 for H–CL to 462.25 cm^{-1} for H–CL (UlS) indicates a decrease of pore opening by sonication.

The weak band detected at 603.46 cm^{-1} for zeolites H–CL is assigned to bending vibrations between tetrahedrons, particularly, to double ring vibration [27, 28].

The shifting of the wave number of the strongest band at 1083.44 cm^{-1} (of asymmetric stretching vibrations of the internal (Al,Si)O$_4$ tetrahedrons) to the low-frequency band at 1079.65 cm^{-1} is associated, apparently, with a decrease in the relative content of Si/Al ratio in zeolite framework [15, 29, 30], with the increase in the length of the bonds Si–O–Si(Al) [31, 32] and with the formation of structured effects. It is in good agreement with our data of XRD about reduction of crystallinity of sonicated catalyst H–CL (UlS), and also with already specified and other researches [23, 33].

3.2. Particle Size Distribution

In initial and sonicated catalysts, respectively, in H–CL and H–CL (UlS) particle size distribution with Cumulants and Pade–Laplace inversions algorithms, in terms of intensity and volume was determined. In both cases approximately similar results were received. Particle Polydispersity Index (PDI) had values 0.099 – 0.230, i.e. particle sizes of the sample were not very diverse; there was relatively narrow distribution of particles.
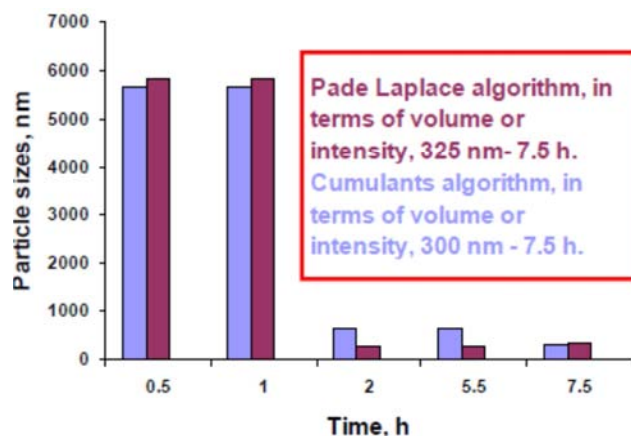

Figure 4. Dependencies of particle sizes of H–CL (UlS) from the time of irradiation of ultrasound.

From the Figure 4 it is visible that at indirect influence of ultrasound on H–CL the average size of particles, equal about 5600 – 5800 nm, sharply decreases after the 2 h induction period, and then it falls almost linearly reaching the size of 300 – 325 nm up to 7.5 h.

3.3. Catalytic Activity

The effect of reaction time ranging from 1 to 10 h at 80 and 120°C on yield of MS showed optimal reaction time of 4 h. During this time a certain state of equilibrium value of the MS yield is attained, and then it decreases because of side

processes. For optimization of esterification reaction conditions the dependences of catalytic activity (conversion of SA, yield and selectivity of MS) on following various factors have been investigated: mass of the catalyst, molar ratio of reagents, and temperature. Results are presented in Figures 5 – 7.

As can be seen from Figure 5 activity of sonicated catalyst is more than the parent H–CL; particularly, with a mass of the catalysts equal to 0.4 g conversion of SA and selectivity to MS over H–CL (UlS) is 90 and 95 %, respectively, but over H–CL – 36.8 and 86.9 %; with growth of mass of catalysts between 0.1 and 0.5 g the conversion of SA and yield of MS for both catalysts increases, but selectivity to MS remains approximately high (about 90 – 97 %) for the parent catalyst and for processed by ultrasound.
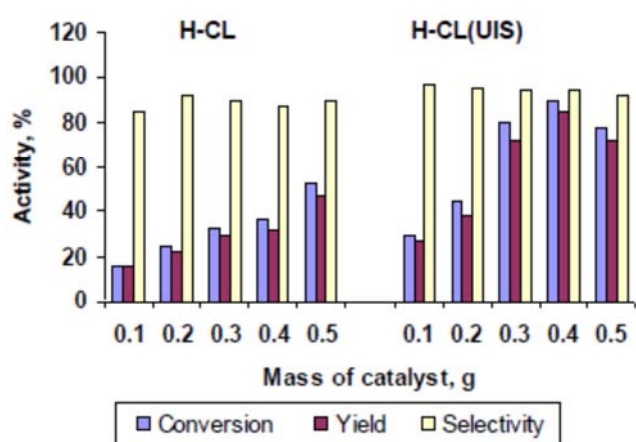

Figure 5. *The effect of mass of catalysts on their catalytic activity (conversion of SA, selectivity and yield of methyl salicylate). Reaction time – 4 h, molar ratio SA / methanol – 1/4, temperature – 120°C.*

As is known, the esterification reaction is a reversible process and for the equilibrium shift to the right one of the components should be taken in excess. From Figure 6 it is seen that for H–CL and H–CL (UlS) with increasing molar ratio of SA / methanol from 1/2 to 1/10 the conversion of SA and MS yield extremely vary and the optimal molar ratio is 1/4. In so doing in case of both catalysts there is high selectivity of MS (87 – 95 %).
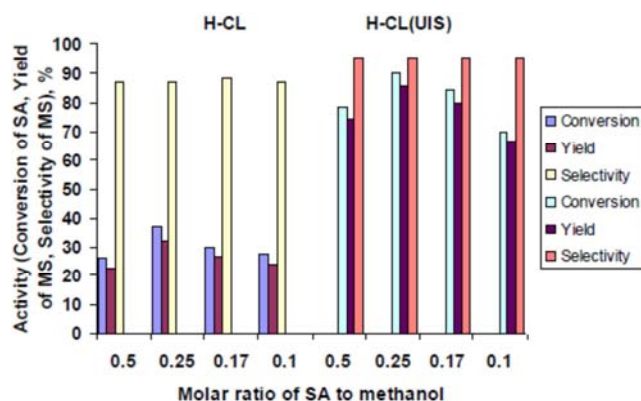

Figure 6. *The effect of molar ratio of SA to methanol on the catalytic activity of H–CL and H–CL (UlS). Reaction time – 4 h, mass of catalysts – 0.4 g, temperature – 120°C.*

Dependence of activity on temperature is shown in Figure 7. It is visible that conversion of SA with a temperature increases. However, the maximum yield of MS on both catalysts is reached at 120°C which on H–CL (UlS) is much higher, 85.5 %, and on H–CL is less, 32 %.
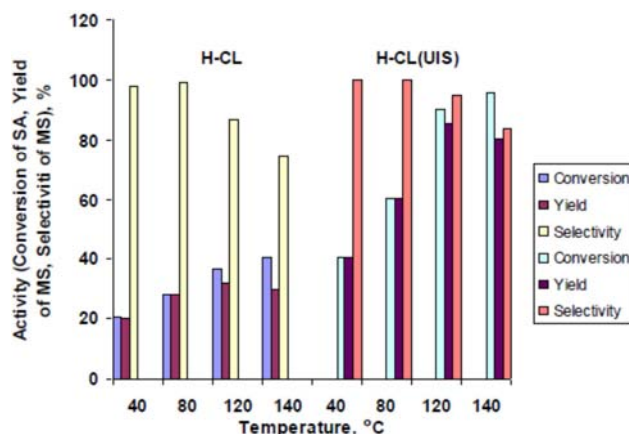

Figure 7. *The effect of temperature on the catalytic activity of H–CL and H–CL (UlS). Molar ratio SA / methanol – 1/4, Reaction time – 4 h, mass of catalysts – 0.4 g.*

Optimal catalyst mass (0.4 g), molar ratio SA / methanol (1/4) and reaction temperature (120°C) were chosen.

In the presence of both studied catalysts: H–CL and H–CL (UlS) the selectivity to methyl salicylate is approximately high, but SA conversion and yield of MS only by the catalyst irradiated with ultrasound are high. It allows assuming that the nature of the active centres of both catalysts is identical, but when processing the catalyst with ultrasound its structural changes have to be connected with the growth of amount and / or strength of the Brönsted acid centres (OH-groups) necessary for carrying out of esterification reaction. On this indirectly specifies also the dependence of activity in esterification of catalysts H–CL and H–CL (UlS) from the sizes of particles. From Figure 8 it is visible that catalytic activity of the catalyst H–Cl (UlS) in the formation of methyl salicylate sharply increases with reduction of the size of its particles from 5636 to about 300 nm.
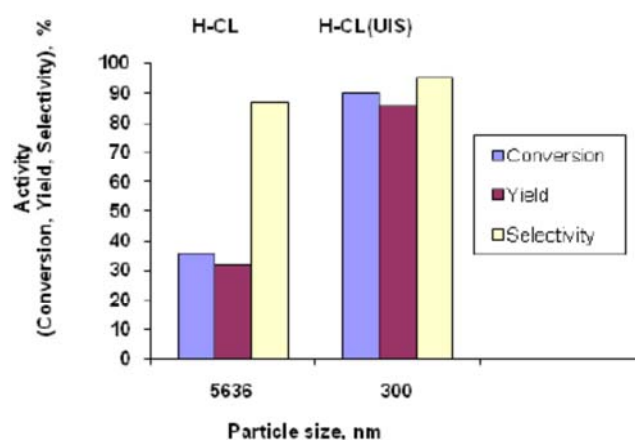

Figure 8. *The dependence of the catalytic activity in the esterification from the particle size of catalysts H–CL and H–Cl (UlS). Reaction time – 4 h, mass of catalysts – 0.4 g, temperature – 120°C.*

The acid form of a natural clinoptilolite processed by ultrasound is almost comparable by catalytic activity with industrial catalyst – sulphuric acid, the most active in reaction of formation of methyl salicylate by esterification; in particular, in the presence of H_2SO_4 at 90 – 100°C conversion of SA and selectivity on methyl salicylate make 85 and 90 %, respectively [16, 34], on H–CL (UlS) – as much at 120°C and on zeolites H–Beta, H–ZSM–5 at 135°C – 49, 44 and 92 % [17].

Reusability of catalysts. In the above described optimal conditions (0.4 g of the catalyst H–CL (UlS), reaction time – 4 h, 120°C) was tested the reuse of the sonicated catalyst. For that, the spent catalyst before repeated application is separated from the reaction mixture by filtration, then it was washed with diethyl ether and water; then it was heated successively in a stream of pure air and helium for 3 h at 300°C. Conversion of SA and yield of MS after threefold use of the catalysts differs from the original an average of 5 – 7 %. This indicates a satisfactory repeatability of activity of sonicated with ultrasound acid form of natural clinoptilolite.

4. Conclusions

1. The catalytic reaction of the esterification of salicylic acid with methanol into methyl salicylate was investigated. The acid form of natural clinoptilolite (of Dzegvi deposit, Georgia) H–CL ($\nu(SiO_2)/\nu(AI_2O_3)$ = 23.3) and the form H–CL (UlS) which was obtained by indirect irradiation with ultrasound (40 kHz, 100 W) of the parent H–CL for 7.5 h were used as catalysts.

2. The research of the catalysts by the methods of FTIR, XRD and by means of the laser light scattering particle size analyzer has shown that the indirect influence of ultrasound on the catalyst H–CL causes the particle size reduction and the structural changes in it; particularly, in the FTIR spectra the shifts of structurally sensitive (603.5 cm^{-1}) and structurally insensitive (465.3 and 1083.4 cm^{-1}) bands, reduction by 8 % of degree of its crystallinity and decrease of the sizes of its particles from 5600 – 5800 to 300 – 325 nm were observed.

3. There was the effect of particle size – as compared with the catalyst H–CL with decreasing particles sizes in the H–CL (UlS) the catalytic activity of the latter in the catalytic esterification drastically increased and the conversion of the salicylic acid and the selectivity to methyl salicylate were very high, 90 and 95 %, respectively, at 120°C. Also the sonicated catalyst H–CL (UlS) is reusable.

4. Comparison with literary data shows that acid form of clinoptilolite processed with ultrasound can be almost compared with catalytic activity of more active sulphuric acid in the esterification for preparation of methyl salicylate and it is more active than zeolites: H–ZSM–5 and H–Beta.

Acknowledgements

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