

CATALIZATORI DE TIP ZEOLIT UTILIZAȚI LA PIROLIZA DEȘEURILOR VEGETALE: SINTEZĂ ȘI CARACTERIZARE

ZEOLITE-TYPE CATALYSTS USED FOR PYROLYSIS OF VEGETAL WASTE: SYNTHESIS AND CHARACTERIZATION

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Pyrolysis and gasification as well as the product upgrading can be performed by conventional heating or microwave heating, the latter being preferred lately due to its advantages, such as fast heating and start-up or short processing time. The resulting products from gasification and pyrolysis have certain limitations and cannot be used for application in their current state. Pyrolysis and gasification are accompanied using catalysts to improve the yields or quality of reaction products.

The main goal of our research was to study the synthesis and structural characterization of ZSM-5 zeolite type catalysts, as well as to simulate their potential behavior in pyrolysis and gasification process of different vegetal waste.

As starting raw material has been used ZSM-5 zeolite that was subjected to protonation to obtain HZSM-5 form of zeolite. Then, substitution of H from protonated form with different transitional metals (Me = Ni, Mo, Co, Fe²⁺, Fe³⁺) was employed. The purpose was to establish the catalytic ability of Me-ZSM-5 substituted zeolite during pyrolysis.

To establish composition and structural-morphological characteristics of Me-ZSM-5 catalysts there were performed X-ray analysis and Fourier Transformed Infrared (FTIR) spectroscopy before and after pyrolysis process. The results have shown the preservation of structural features even after use, confirming their good stability after calcination at 600°C, the simulated temperature of pyrolysis. Morphological analyses have been done using Scanning Electron Microscopy (SEM) together with Energy Dispersive X-ray Analysis (EDAX) for elemental distribution and analysis.

The results were considered satisfactory and the first tests on both thermochemical and microwave assisted pyrolysis seem to be very promising.

Piroliza și gazeificarea precum și îmbunătățirea produselor pot fi realizate prin încălzire convențională sau pe bază de microunde, ultima fiind preferată în ultimul timp datorită avantajelor sale, cum ar fi încălzirea rapidă sau timpul scurt de procesare. Produsele rezultate în urma gazeificării sau pirolizei au anumite limitări și nu pot fi aplicate ca atare. Piroliza și gazeificarea sunt aplicabile eficient prin utilizarea catalizatorilor pentru îmbunătățirea randamentelor sau a calității produșilor de reacție.

Scopul prezentei lucrări s-a axat pe sinteza și caracterizarea structural-morfologică a catalizatorilor de tip ZSM-5, precum și simularea comportării lor potențiale în procesele de piroliză și gazeificare a unor deșeuri vegetale.

Ca materie primă s-a utilizat zeolitul tip ZSM-5 care a fost supus protonării pentru a se obține forma HZSM-5. Apoi, s-a realizat substituția hidrogenului din forma protonată cu diverse metale tranziționale (Me = Ni, Mo, Co, Fe²⁺, Fe³⁺). Scopul a fost de a se stabili abilitatea catalitică a zeolitelui substituit Me-ZSM-5 în timpul pirolizei. Pentru a se determina caracteristicile structural-morfologice a catalizatorilor Me-ZSM-5 s-au efectuat analiza de difracție de raze X și analiza spectroscopică în infraroșu (FTIR). Rezultatele au evidențiat păstrarea caracteristicilor înainte chiar și după piroliză confirmând stabilitatea structurală după calcinare la 600°C, temperatura utilizată pentru simularea procesului. Analiza morfologică s-a realizat prin intermediul microscopiei electronice de baleiaj (SEM) alături de spectroscopia de dispersie a energiei de raze X (EDAX) pentru determinarea compoziției și distribuției elementale.

Rezultatele sunt considerate ca fiind satisfăcătoare iar primele teste realizate în procesul de piroliză atât termochimic cât și asistat de microunde par a fi extrem de promițătoare.

Keywords: pyrolysis, catalyst, zeolite, synthesis ZSM-5

1. Introduction

Due to the high demand for energy worldwide and unreliable fossil fuel prices, significant R&D efforts are focused on other sources of energy. Biofuels derived from lignocellulosic biomass, commonly known as second generation biofuels can overcome most of the limitations posed by first generation biofuel (ethanol and bio-diesel) derived from food sources. A wide variety of biomass in different parts of the world can be utilized for biofuel synthesis, including agricultural waste, organic residue, grassy and woody biomass along with

dedicated biofuel crops.

Thermochemical and biochemical conversion is a common route for conversion of biomass to desired bioproducts [1]. Pyrolysis and gasification offer reliable sources of energy in the form of syngas, bio-oil and biochar from agricultural, forest and municipal waste. Gasification is a thermochemical degradation of biomass to form syngas through series of chemical reactions at high temperatures (700–1100 °C) and controlled oxygen environment. Gasification is performed in the presence of steam or partial air pressure. Pyrolysis is a thermoche-

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mical decomposition of biomass to produce liquid fuel in total absence of oxygen [2]. Pyrolysis temperature is lower than gasification ranging from 400 to 700 °C [3]. Products from gasification and pyrolysis have certain limitations and cannot be used for application in their current state. These limitations include low heating value, higher oxygen content and higher impurities amongst others.

Catalysts play a crucial role in pyrolysis and gasification processes. Main purpose of catalytic pyrolysis is the removal of oxygenated compounds and cracking high molecular weight products to lower chain compounds [4]. Depending on the desired products, various types of catalysts are used. Zeolites improve aromatics yield [5 - 7], while metal oxides and carbon-based catalysts increase syngas production [8-10].

Zeolites are among the most used types of catalysts. They have many applications and their catalytic activity is related to their shape selectivity and acidity [4]. ZSM-5 zeolite is an effective deoxygenation catalyst [4].

Zeolites have been shown to be effective in bio oil up-grading via deoxygenation of pyrolysis vapors and promoting formation of aromatic hydrocarbons. The mechanism of bio oil upgrading when using zeolites include series of reactions such as decarboxylation, dehydration, decarbonylating and aromatization [11], resulting in formation of hydrocarbon rich fuel. Fan et al. [6] described the advantages of using zeolites in pyrolysis processes. They noted that the acidic strength and pore size of the zeolite plays an important role in bio oil upgrading. The acidity of the zeolite increases as the Si/Al ratio decreases and the aromatization ability of zeolites also increases. There are many types of zeolites used as catalysts, including HZSM-5, H-Ferrierite, H-mordenite, HY, however HZSM-5 has been found to have stronger acidity and thus is most widely applied to produce deoxygenated compounds.

The main goal of our research was to study the synthesis and structural characterization of ZSM-5 zeolite type catalysts, as well as to simulate their potential behavior in pyrolysis and gasification process of different vegetal waste (in our case straws of rapeseed and poplar). The purpose was to establish the catalytic ability of Me-ZSM-5 substituted zeolite during pyrolysis.

2. Experimental

2.1 Materials and methods

2.1.1. Synthesis of protonated ZSM-5 zeolite

As starting raw material has been used ZSM-5 zeolite that was subjected to protonation to

obtain HZSM-5 form of zeolite. Then, substitution of H from protonated form with different transitional metals (Me = Ni, Mo, Co, Fe²⁺, Fe³⁺) was employed.

In order to obtain the doped zeolite of type Me-ZSM-5 it was initially used Na-ZSM-5 zeolite bought from Sigma Aldrich (ACS quality). The sodium salt of zeolite was subjected to protonation following when an ion-exchange method was employed according to the next steps:

- Materials used in the initial stage were Na-ZSM-5; NH₄Cl; double distilled water;
- 90 g Na-ZSM-5, 10.68 g NH₄Cl and 200 ml double distilled water (deionized) were added in a round-bottom flask that was sealed with a rubber stopper and left under stirring until homogenization of solution;
- Then the round-bottom flask with the obtained solution was heated for 4 hours at ~105 °C, under constant stream of Ar;
- Further, the solution was kept under stirring for the next 24 hours, without Ar flow and heat, but still sealed (so in controlled environment).

Once the ion exchange was accomplished the solution has been centrifuged for 10 minutes at 60 rot/min until the solid obtained is separated from the liquid phase. To remove completely the residual chlorine the recovered solid has been washed several times with distilled water up to formation again of a solution, followed by centrifugation. The procedure was repeated several times.

Finally, the precipitate has been dried directly in the tubes used for centrifugation, at 85°C for 24 hours and then the half-dried solid phase was collected and dried until the mass was less than initial mass of 90 g. Performing appropriate calculations has been found a conversion rate of Na to H around 80%, in agreement with literature data.

2.1.2. Synthesis of Me-ZSM-5 catalysts

The Me-ZSM-5 catalysts were prepared following a wet method for impregnation with transitional metals. This reaction was employed in order to upload the H-ZSM-5 surface network with different transitional metals, namely Ni(2+), Mo(6+), Co(2+), Fe(2+) and Fe(3+). The uploading was performed through a usual wet impregnation method using some small changes. In the present case the solution of the metallic salt was not allowed to evaporate from the support and instead centrifugation was used to remove the solution in excess. There were tested multiple stirring methods including sonication, slow or fast stirring with the purpose de establish optimum conditions of mixing in future reactions.

As raw materials for the transitional metal dopants were used the following precursors

$\text{Fe}^{(+2)}\text{Cl}_2$, $\text{Fe}^{(+3)}\text{Cl}_3$, $\text{Co}^{(+2)}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$, $(\text{NH}_4)_6\text{Mo}^{(+6)}\text{O}_{24} \cdot 4(\text{H}_2\text{O})$, $\text{Ni}^{(+2)}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$, deionized water (double distilled), methanol and H-ZSM-5 as prepared. All these precursors added in different amounts to get a final metal absorption of 1.5%.

The general method for preparation of Me-ZSM-5 is given by the next steps:

1. Appropriate amount of Me-precursor is added in deionized water and mixed by sonication to assure complete dissolution;
2. It is added a certain amount of the obtained zeolite support (HZSM-5) in deionized water and subjected to mixing using magnetic stirring;
3. The solution prepared at first step (based on Me-precursor) is then added drop by drop with the aid of a pipette in the solution from stage 2 (containing zeolite support) while is continuously magnetic stirred;
4. A certain amount of methanol is then added directly in the mixture obtained in step 3;
5. The whole prepared mixture (steps 3 and 4) is sealed off (reaction vessel was closed with a stopper) and left under magnetic stirring for the next 24 hours to get an accurate impregnation.
6. Next day the solution from step 5 is centrifugated for 10 minutes at 60 rotations/minute, separating the obtained solid phase from the remained liquid. For an effective wash the recovered solid is subjected to several cycles of washing with distilled water followed by centrifugation.
7. The ultimate precipitated solid phase (from step 6) is initially dried at 85°C for 24 hours directly in the tubes used at centrifugation and then the half-dried precipitate is collected and dried again, until the mass is less than that of the initial mass of the support.
8. The dried precipitate is then calcined at 500°C for 4 hours at a heating rate of 5°C/min, thus resulting an overall time of 5.5 hours.

9. The final product is Me-ZSM-5 catalytic zeolite.

The procedure described is almost similar for all precursors with very slight difference as regard the drying time in the case of Mo-ZSM-5.

3. Results and discussions

For the characterization of the samples, in Table 1 there are listed all obtained doped catalysts and their codes, as well. Also, all the samples were heat treated (calcined) at 600°C in order to simulate the pyrolysis process temperature and thus to forecast their potential structural behavior.

3.1. Materials characterization

3.1.1. Structural characterization

X-ray diffraction analysis

X-ray diffraction analyses were carried out using an Empyrean X-ray diffractometer (manufactured by PANalytical the Netherlands), using a $\text{K}\alpha_1$ ($\lambda = 1.540598$) Cu radiation, equipped with two bounce Ge hybrid monochromator (220) for Cu and a PIXcel3D detector

After preparation of all samples it was performed the X-ray analysis (XRD) of the resulting potential catalysts in order to identify the crystalline phases and to compare possible effects of the doping transitional metals on the structural network of the zeolite.

As reference was considered the as-received ZSM-5 zeolite before all physical, chemical and heat treatments. All the samples, irrespective of the dopant element, heat treated or not presented extremely similar X-ray diffraction patterns, including the reference one. In Figure 1 are given several X-ray patterns for some of the catalysts, pre-calcined or post calcined and having different dopants. The overlapping is obvious. It can be concluded that insertion of the transitional metals within the network of the ZSM-5 zeolite, as well as the applied heat treatment to simulate catalyst behavior at pyrolysis temperature do not impar upon the structure and its stability.

Table 1

Zeolite types and their codes / Tipul zeoliților și codurile lor

Code	Type	Treatment
A0a	ZSM-5	Pre-calcined
A1a	HZSM-5	Pre-calcined
A2a	Ni-HZSM-5	Pre-calcined
A3a	Mo-HZSM-5	Pre-calcined
A4a	Co-HZSM-5	Pre-calcined
A5a	Fe(2+)-HZSM-5	Pre-calcined
A6a	Fe(3+)-HZSM-5	Pre-calcined

Code	Type	Treatment
A0b	ZSM-5	Post-calcined
A1b	HZSM-5	Post-calcined
A2b	Ni-HZSM-5	Post-calcined
A3b	Mo-HZSM-5	Post-calcined
A4b	Co-HZSM-5	Post-calcined
A5b	Fe(2+)-HZSM-5	Post-calcined
A6b	Fe(3+)-HZSM-5	Post-calcined

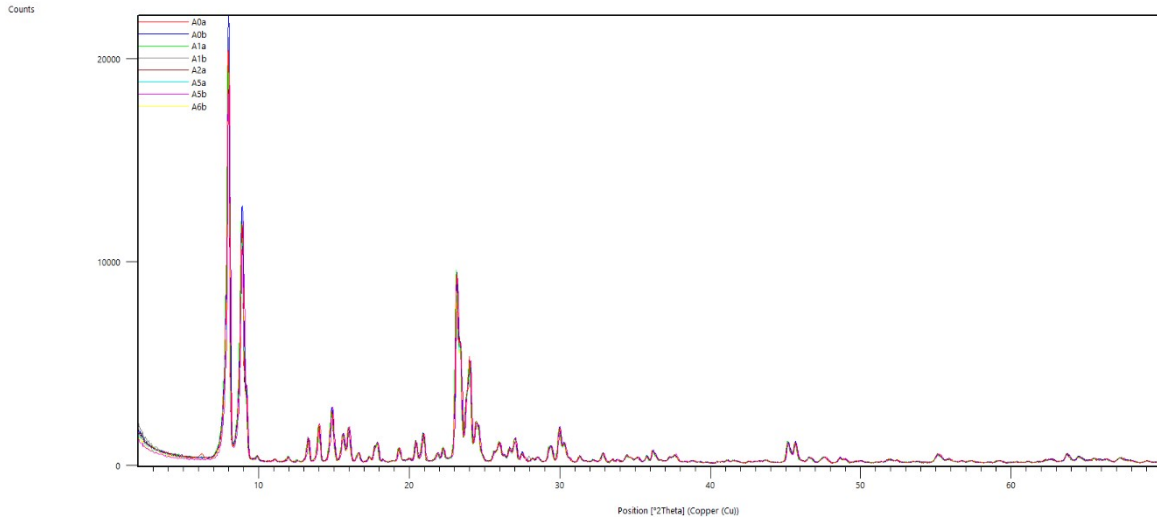


Fig. 1 - X-ray diffraction patterns of some Me-ZSM-5 catalysts / *Difractogramele unora dintre catalizatorii Me-ZSM-5.*

Fourier-transform infrared spectroscopy (FTIR)

Complementary to X-ray diffraction method, FTIR method can provide additional information regarding the degree of disorder within the network or structural distortions and possible damages.

The FTIR spectra have been recorded using KBr pellets in the range $400\text{-}4000\text{ cm}^{-1}$ with a Thermo Nicolet 6700 spectrometer provided with OMNIC software and a sensitivity of 4 cm^{-1} . For pellets preparation 1 mg of sample and 200 mg KBr were homogenized with a magnetic homogenizer and then pressed with a force of 1000 N/cm^2 in a Carl Zeiss press.

As in the case of X-ray diffraction method, the similarity of IR spectra for all samples is again obvious and thus confirming the stability of catalyst. The dopants effects are missing showing that there is no influence upon the structure of Me-ZSM-5.

For comparison there are given two spectra of $\text{Fe}^{(2+)}\text{-ZSM-5}$, both pre-calcined and post calcined in figure 2 (a and b).

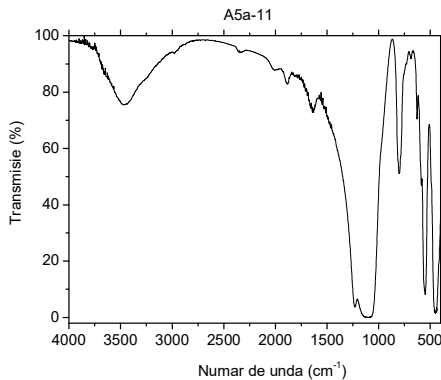


Fig. 2 a. - Spectrum of pre-calcined $\text{Fe}^{(2+)}\text{-ZSM-5}$ / *Spectrul FTIR al catalizatorului $\text{Fe}^{(2+)}\text{-ZSM-5}$ precalcinat.*

In Table 2 there given the assignment of transmission peaks of several samples' spectra.

Very few differences can be notice between some pre-calcined and post calcined catalysts as concern the vanishing of some vibrations of hydroxyl group and that can be explained through that the heat treatment made diminishing of residual water content still present at lower temperature (pre-calcined state).

3.1.2. Morphological characterization

Scanning electron microscopy (SEM)

Scanning electron microscopy analyzes were performed using a FEI Company's Quanta Inspect F microscope with field emission electron beam gun (FEG) and a resolution of 1.2 nm equipped with an energy dispersive X-ray spectrometer (EDAX) with a Mn eq of 129 eV.

There were analyzed from morphological view point all the catalysts in protonated form as well as doped with transitional metal ions (Ni^{2+} ,

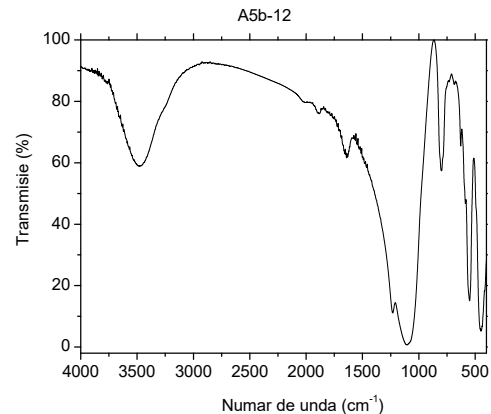


Fig. 2 b - Spectrum of post-calcined $\text{Fe}^{(2+)}\text{-ZSM-5}$ / *Spectrul FTIR al catalizatorului $\text{Fe}^{(2+)}\text{-ZSM-5}$ postcalcinat*

Table 2

Assignments of the IR transmission bands detected in catalysts pre-calcined and post calcined
Atribuirea benzilor de transmisie IR pentru catalizatorii pre și post calcinați

Bands of IR spectra								Atribuirii
Sample A0a	Sample A0b	Sample A1a	Sample A1b	Sample A2a	Sample A5a	Sample 5b	Sample A6b	
	3763				3750	3760	3762	v (O-H) in silanol Si-OH groups
3680	3682						3682	v (O-H) in silanol Si-OH groups
3660	-	3656	3656	-	3650	-	3665	v (O-H) in Al-OH
							3644	
3457	3469	3457	3470	3470	3467	3477	3471	v (O-H) in silanol Si-OH groups
-	-	3232	-	-	-	-	-	v (O-H)
-	-	3117	-	-	-	-	-	v (O-H)
2975	-	2982	-	-	2979	-	-	v (C-H) in CH ₂
2007	2007	2013	2007	2007	2007	2007	2007	
1886	1886	1885	1882	1884	1882	1885	1882	
					1655			v (O-H)
1640	1640	1640	1640	1640	1640	1640	1640	v (O-H)
-	-	1405 u	-	-	-			
1231	1231	1231	1231	1228	1231	1231	1231	v (Si-O-Si)
1108	1108	1104	1108	1112	1096	1104	1104	v (Si-O-Si)
800	800	800	802	802	802	797	798	v (Si-O)/v (Al-O)
730	728	726	730	730	733	733	733	v (Al-O) in AlOH
686	686	686	686	686	686	689	686	v (Al-O) in AlOH
-	-	-	-	-	-	-	630	v (Al-O) in AlOH
628	628	628	628	628	628	628	628	v (Al-O) in AlOH
586	586	586	586	586	586	586	586	v (Al-O)
549	549	549	549	549	549	549	549	v (Al-O)
451	446	451	451	452	448	448	451	v (Si-O)
411 u	411 u	-	-	-	436u	436 u	-	

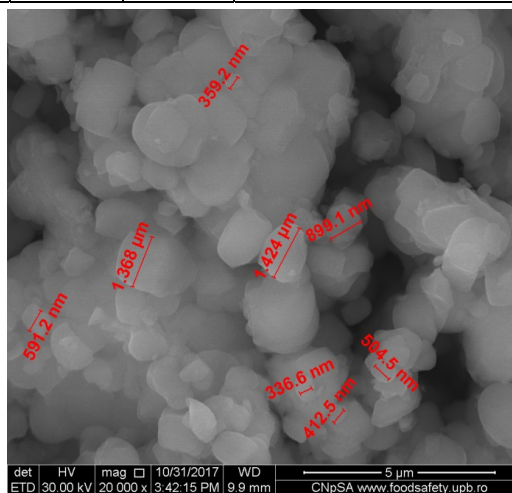
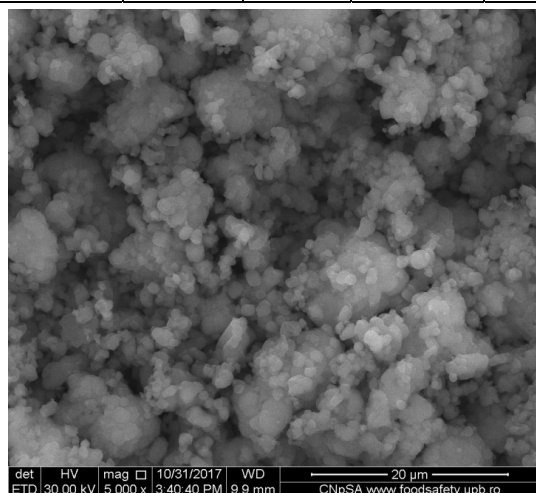


Fig. 3(a) - SEM micrograph of pre-calcined HZSM-5 / *Micrografie SEM a HZSM-5 precalcinat.*

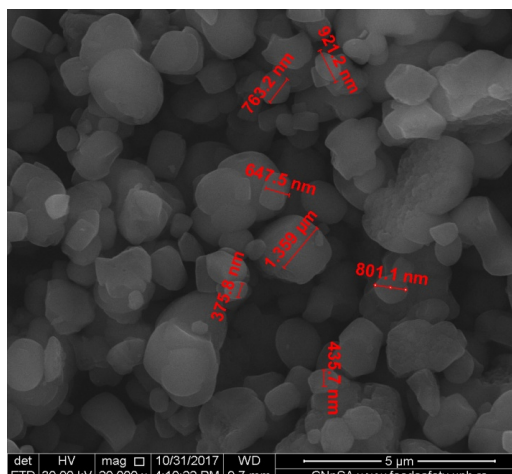
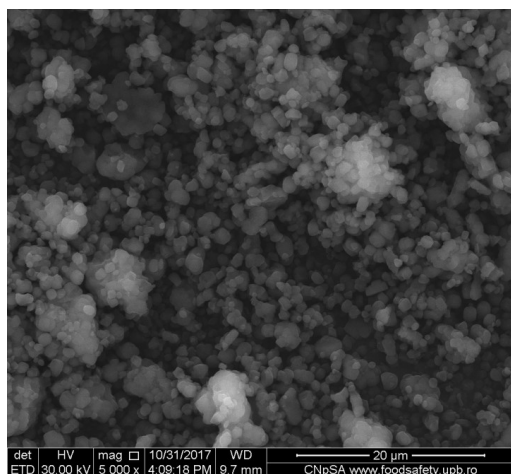


Fig. 3b) - SEM micrograph of post-calcined HZSM-5 / *Micrografie SEM a HZSM-5 post calcinare.*

Co²⁺, Mo⁶⁺, Fe²⁺, Fe³⁺). Also, a comparison between pre-calcined and post-calcined obtained catalysts was performed. To get a good resolution of the micrographs all samples were covered with a thin layer of gold for SEM analysis.

As a general remark, a morphological behavioral pattern was found for all Me-ZSM-5 catalysts both for pre-calcined and post calcined samples. Thus, in pre-calcined catalysts the zeolite grains are almost uniformly distributed, having regular shapes with straight edges. The pre-calcination treatment led to an agglomeration of zeolite grains which dimensions range between 400 – 1500 nm, as seen, for example, in Figure 3a for HZSM-5 pre-calcined.

After post-calcination treatment a weathering process of the larger agglomerates can be observed. However, the regular geometric shape of the grains looks not to be affected by post-calcination and the dimensional range of the grains it is somehow preserved constant as

compared with pre-calcination stage. This is a clear indication that in fact we have to deal exclusively with a disaggregation and “detachment” process of the smaller zeolite particles from the larger ones without affecting their inner structure as observed from X-ray and FTIR analyses. (see Figure 3b for HZSM-5 post-calcined) and not a damage of the initial structure.

This structural-morphological pattern is actually recovered for all zeolite catalysts obtained and heat treated. To prove this finding in Figure 4 (a) and (b) there presented the corresponding micrographs for Ni-ZSM-5 sample, pre-calcined and post-calcined, as well. The similarities are so obvious, thus supporting that doping and applied heat treatments do not affect the initial structure. Grain size dimensional range is almost the same between pre-calcined and post-calcined catalyst and this observation remains valid for all zeolites Me-ZSM-5 synthesized in present work.

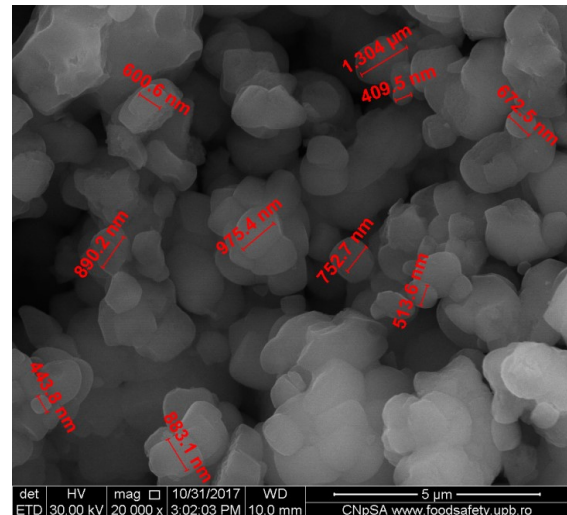
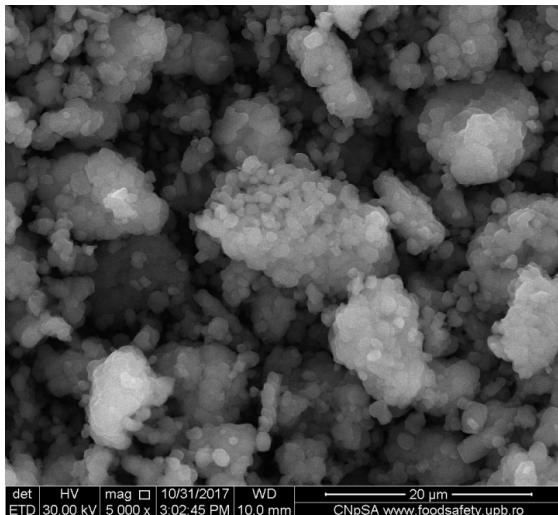


Fig. 4(a) - SEM micrograph of pre-calcined Ni-ZSM-5 catalyst / *Micrografie SEM a Ni-ZSM-5 precalcinat*

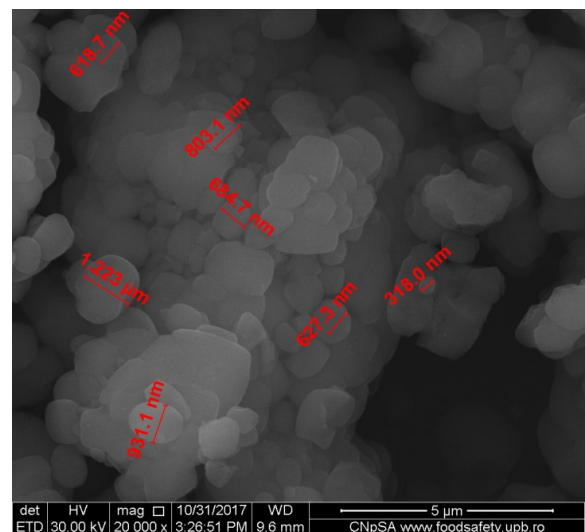
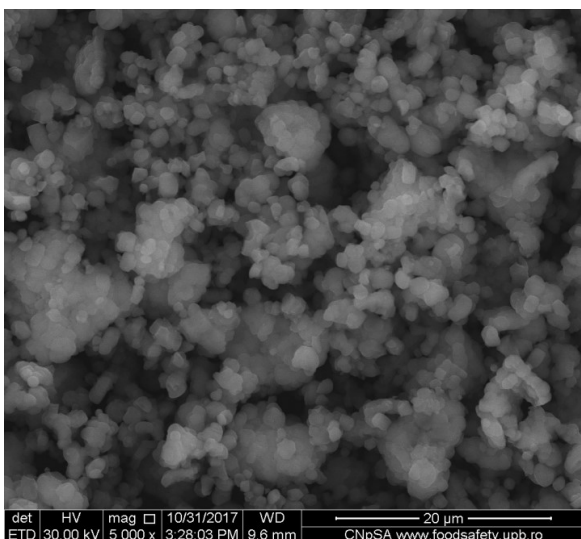


Fig. 4(b) - SEM micrograph of post-calcined Ni-ZSM-5 catalyst / *Micrografie SEM a Ni-ZSM-5 postcalcinat*.

Energy dispersive X-ray spectroscopy (EDAX)

If structural and morphological behavior as proved by means of X-ray, FTIR and SEM analyses is essentially similar for all zeolite catalysts, the compositional one has been studied

based on EDAX spectroscopy. In the next Figures (5a,b, 6a) there are presented, for example, the EDAX spectra for both HZSM-5 pre/post calcined and Ni- ZSM-5 pre/post calcined (Fig. 6b).



Fig. 5(a)- EDAX spectrum of pre-calcined HZSM-5 catalyst / Spectrul EDAX a catalizatorului HZSM-5 precalcinat.



Fig. 5(b) - EDAX spectrum of post-calcined HZSM-5 catalyst / Spectrul EDAX a catalizatorului HZSM-5 postcalcinat.



Fig. 6(a) - EDAX spectrum of pre-calcined HZSM-5 catalyst / Spectrul EDAX a catalizatorului Ni-ZSM-5 precalcinat.

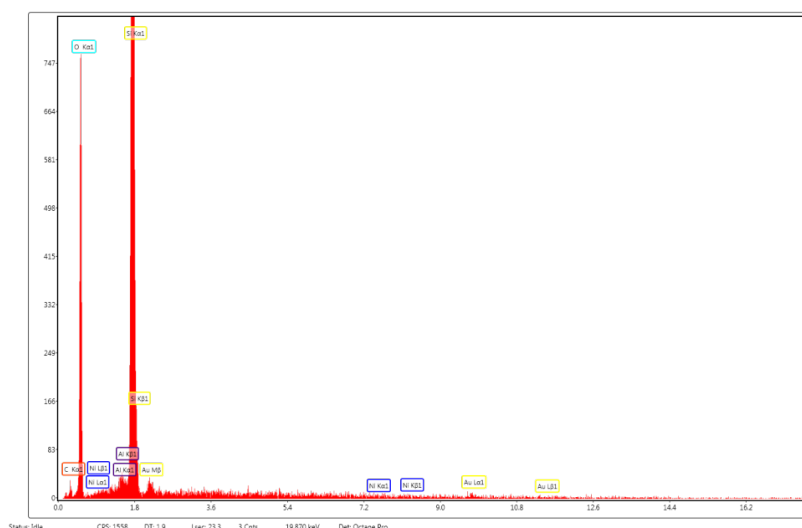


Fig. 6(b) EDAX spectrum of post-calcined Ni-ZSM-5 catalyst // Spectrul EDAX a catalizatorului Ni-ZSM-5 postcalcinat.

One can see the specific lines of Si, Al and O in both figures, that are almost identical. In this case it is clear that no alteration of the chemical composition due to applied heat treatments occur, that means preservation of the initial not only of structure and morphology as well, but of chemical composition, too.

In the case of Ni-ZSM-5 catalyst, as seen in Figure 6, can be also detected the spectral lines of Nickel near the ones for Al, Si and O. Again, the similarity of both spectra is obvious confirming the stability of the catalyst. This behaviour can be found for all the other studied Me-ZSM-5 zeolite catalysts.

4. Conclusions

The purpose of our research was to study the synthesis and structural characterization of Me-ZSM-5 zeolite type catalysts, as well as to simulate their potential behavior in pyrolysis and gasification process of different vegetal waste.

The syntheses of Me-ZSM-5 catalysts were performed based on a well-established protocol described in the paper, for each type of transitional metal used as doping element. Reproducibility of wet chemical synthesis method has been verified successfully.

The obtained potential catalysts were characterized from structural, morphological and chemical stability view point. A post-calcination heat treatment was subjected to all doped zeolites at 600°C with the purpose to simulate the thermal conditions of pyrolysis process and to check the stability of the catalysts. All analyses performed have emphasized an excellent chemical, structural and morphological stability for all potential catalysts. Future studies will be devoted to test the catalytic aptitude in real pyrolysis process.

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