

SYNTHESIS AND CHARACTERIZATION OF MONTMORILLONITE-BASED CATALYSTS FOR VEGETAL WASTE PYROLYSIS

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For present time, declining petroleum resources, accompanied by an increasing demand for oil and chemicals by emerging economies, as well as environmental and political concerns about fossil fuels, it has become essential to develop energy-efficient processes for the sustainable production of fuels and chemicals using alternative resources. In this respect, biomass (including vegetal waste from different industries and agriculture) is considered the renewable energy source with the highest potential regarding energy needs of modern society, for both the developed and developing economies. It represents a sustainable source of organic carbon and biofuels, which generate significantly fewer greenhouse gas emissions than fossil fuels, and can even be neutral in CO₂ production balance, when efficient methods are developed.

Regarding the technologies for vegetable biomass valorization, fast pyrolysis is one of the most viable perspectives, if the quality of the products (gas, liquid and char) is improved.

Pyrolysis and gasification as well as the product upgrading can be performed by conventional heating or microwave heating. Both processes require the use of catalysts to improve the yields or quality of reaction products. The purpose of present paper was to establish the catalytic ability of montmorillonite (MMT) after doping with different transitional metals (Me = Ni, Mo, Co, Fe²⁺, Fe³⁺), following a procedure developed in a previous paper [1].

There were performed X-ray diffraction analysis and Fourier Transformed Infrared (FTIR) spectroscopy before and after pyrolysis process upon the Me-MM catalysts to verify composition and to establish their structural and morphological characteristics. Morphological characteristics were determined by Scanning Electron Microscopy (SEM) together with Energy Dispersive X-ray Analysis (EDAX) for elemental distribution and analysis.

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 and were considered satisfactory and the initial tests on both thermochemical and microwave assisted pyrolysis seem to be promising.

În prezent, scăderea resurselor petroliere, însoțită de o cerere crescândă de petrol și produse chimice de către economiile emergente, precum și preocupările de mediu și politice cu privire la combustibilii fosili, a devenit esențială dezvoltarea proceselor eficiente din punct de vedere energetic pentru producția durabilă de combustibili și produse chimice folosind resurse alternative. În acest sens, biomasa (inclusiv deșeurile vegetale din diferite industrii și agricultură) este considerată sursa de energie regenerabilă cu cel mai mare potențial în ceea ce privește nevoile energetice ale societății moderne, atât pentru economiile dezvoltate, cât și pentru cele în curs de dezvoltare. Reprezintă o sursă durabilă de carbon organic și biocombustibili, care generează semnificativ mai puține emisii de gaze cu efect de seră decât combustibilii fosili și poate fi chiar neutră în echilibrul producției de CO₂, atunci când sunt dezvoltate metode eficiente.

În ceea ce privește tehnologiile de valorificare a biomasei vegetale, piroliza rapidă este una dintre cele mai viabile perspective, în cazul în care calitatea produselor (gaz, lichid și cărbune) este îmbunătățită.

Piroliza și gazificarea, precum și modernizarea produsului pot fi realizate prin încălzire convențională sau încălzire cu microunde. Ambele procese necesită utilizarea catalizatorilor pentru a îmbunătăți randamentele sau calitatea produselor de reacție. Scopul prezentei lucrări a fost de a stabili capacitatea catalitică a montmorillonitului (MM) după dopare cu diferite metale tranziționale (Me = Ni, Mo, Co, Fe²⁺, Fe³⁺), urmând o procedură descrisă într-o lucrare anterioară [1].

Au fost efectuate analize de difracție cu raze X și spectroscopie în infraroșu cu transformată Fourier (FTIR) înainte și după procesul de piroliză pe catalizatorii Me-MM pentru a verifica compoziția și pentru a stabili caracteristicile lor structurale și morfologice. Caracteristicile morfologice au fost determinate prin microscopie electronică de baleiaj (SEM) împreună cu analiza cu raze X dispersivă a energiei (EDAX) pentru distribuție și analiză elementală.

Rezultatele au arătat păstrarea caracteristicilor structurale chiar și după utilizare, confirmând stabilitatea lor bună după calcinare la 600°C, temperatura simulată a pirolizei și au fost considerate satisfăcătoare, iar testele inițiale atât pe piroliza termochimică, cât și pe cea cu microunde asistată par a fi promițătoare.

Keywords: pyrolysis, catalyst, synthesis, characterization doped montmorillonite

1. Introduction

Pyrolysis and gasification as well as the product upgrading can be performed in several

ways, 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 products resulting from

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gasification and pyrolysis have certain limitations and cannot be used for application in their current state. Therefore, gasification and pyrolysis are accompanied using catalysts to improve the yields and quality of reaction products, as well.

Due to the high demand for energy worldwide and unreliable fossil fuel prices, significant R&D efforts are focused on different or alternative 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 biodiesel) derived from food sources. A wide variety of biomass in different parts of the world can be utilized for biofuel synthesis, including organic residue, agricultural waste, grassy and woody biomass along with dedicated biofuel crops.

Biochemical and thermochemical conversion is now a common route for conversion of biomass to requested bioproducts [2]. Both 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. Pyrolysis is a thermochemical decomposition of biomass to produce liquid fuel in total absence of oxygen [3]. Pyrolysis temperature is lower than gasification ranging from 400 to 700 °C [4]. 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 [5]. Depending on the desired products, various types of catalysts are used. Alumino-silicates are among the most studied ones. Zeolites improve aromatics yield [6,7,8], while metal oxides and carbon-based catalysts increase syngas production [9,10]. They have many applications and their catalytic activity is related to their shape selectivity and acidity [5].

Alumino-silicates 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 alumino-silicates include series of reactions such as decarboxylation, dehydration, decarbonylating and aromatization [11], resulting in formation of hydrocarbon rich fuel. Fan et al. [7] 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. Clay minerals have been used as the catalysts in laboratory as well as on industrial scale for decades as indicated by several review papers published on this topic [12,13].

Clay minerals catalyze various organic reactions either in the pristine form or in the differently modified versions obtained by protonation of clay mineral with acids, exchange reactions with inorganic cations (Cr^{3+} , Al^{3+} , Cr^{3+} , Cu^{2+} ...) [12], polyoxocations of Al13, GaAl12 [14].

An important and poorly studied group of catalysts used in the pyrolysis of vegetal waste are clays, including montmorillonites, that could receive considerable attention due to their acidic properties. Montmorillonite (MMT), the most common smectite-group clay mineral on the Earth's surface, is also the most used among different clays. This is partly due to the existence of huge deposits, which produce usable material at very low costs, and mainly to its extraordinary adsorption, acidity and cation exchange properties. These characteristics permit various applications, such as pollutant removal from waste waters, polymer composite reinforcement, catalysis, drug release and ionic conductance.

Montmorillonite is one of the most intensely explored catalytic material in heterogeneous catalysis, due to its low cost and ecological character. It also possesses unique properties, such as the ability to exchange cations and the ability to swell, therefore adapting to different species of guests in the intermediate layers [8]. A clay catalyst, montmorillonite K10, is industrially available in large quantities. Montmorillonite is reported as non-corrosive, environmentally friendly, cheap, easy of handling and regenerable solid catalyst.

The main goal of present paper was to perform the synthesis and structural characterization of substituted montmorillonite type catalysts, as well as to simulate the potential behaviour 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-MMT substituted catalysts during pyrolysis.

A montmorillonite material (K10) was doped with different transitional metal ions (Mo^{6+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+}) in order to obtain appropriate catalysts. These catalysts introduced into the reaction medium in small or very small quantities, changing the rate, enter the chemical reaction at a certain stage, but which at the end of the reaction are found in the initial quantity without undergoing any chemical transformation and not affecting in any way negative

environment, helping to preserve it.

2. Experimental

2.1 Materials and methods

In the experimental part we present the impregnation of montmorillonite with transition metals in order to obtain catalysts, which are analyzed by the following methods: Infrared spectroscopy (FTIR), scanning electron microscopy (SEM) with Energy Dispersive X-ray Analysis (EDAX) for elemental distribution and analysis and X-ray diffraction (X-ray) analysis.

The FTIR spectra have been recorded using KBr pellets in the range 400-4000 cm^{-1} with a Thermo Nicolet 6700 spectrometer provided with OMNIC software and a sensitivity of 4 cm^{-1} .

Scanning electron microscopy analyses 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

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.

The natural raw materials montmorillonite (K10) and the following transition metals will be used as raw materials: Ni, Co, Mo and Fe in the form of soluble salts. All raw materials were bought from Sigma-Aldrich (ACS quality).

2.2. Preparation of Me-MMT catalysts

To obtain the following compounds: Ni^{+2} -MMT, Co^{+2} -MMT, Mo^{+6} -MMT, Fe^{+2} -MMT,

Fe^{+3} -MMT, the next steps were followed:

- In the first stage as raw materials for the transitional metal dopants were used the following precursors $\text{Fe}^{(+2)}\text{Cl}_2$, $\text{Fe}^{(+3)}\text{Cl}_3$, $\text{Co}^{(+2)}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$, $(\text{NH}_4)_6\text{Mo}^{(+6)}_7\text{O}_{24} \cdot 4(\text{H}_2\text{O})$, $\text{Ni}^{(+2)}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ with various weights, methanol and 10 mL of deionized

water were added to ensure complete solubility and, the process took place with mixing by sonication.

- In the second stage, 30 grams of purchased montmorillonite K10 were used, and they were dispersed by magnetic stirring in 100 mL of deionized water.

- In the third step the solution from step 1 was added drop by drop using a pipette to the suspension from step 2 (MMT suspension) while it was under magnetic stirring.

- In the fourth step, an amount of 30 mL of methanol was added to the mixture in the third step.

- In the fifth step, the entire mixture thus obtained (steps 3 and 4) was isolated (the reaction vessel was closed with a stopper) and left under magnetic stirring for 24 hours to ensure proper impregnation.

- In the sixth step the suspension resulting in the fifth step was centrifuged for 10 minutes at 60 rpm and the solid obtained was separated from the remaining liquid. For an efficient wash the recovered solid was washed several times with distilled water (distilled water was added over the solid until a solution was formed again, then centrifuged again).

- In the seventh step, the deposit obtained from the successive washes from step 6 was first dried at 105 °C for 24 hours directly in the tubes used for centrifugation and then the semi-dry precipitate was collected and dried again. until the remaining mass was less than the initial mass of the support (30g).

- In the eighth stage the dry precipitate was then calcined at 600 °C for 4 hours having a heating rate of 5 grd / min , thus resulting in a total time of approximately 5.5 hours. As a result of which the following compounds were obtained: Ni^{+2} -MMT, Co^{+2} -MMT, Mo^{+6} -MMT, Fe^{+2} -MMT, Fe^{+3} -MMT.

3. Results and discussions

For the characterization of the samples, in Table 1 there are presented the 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 higher temperature and thus to forecast their potential structural behaviour.

Table 1

Doped-montmorillonite types and their codes/ Tipurile de montmorilonit dopați și codificarea lor		
Code	Type	Treatment
B0a	MMT stock (K10)	Pre-calcined
B1a	Ni-HZSM-5	Pre-calcined
B2a	Mo-HZSM-5	Pre-calcined
B3a	Co-HZSM-5	Pre-calcined
B4a	Fe(2+)-HZSM-5	Pre-calcined
B5a	Fe(3+)-HZSM-5	Pre-calcined

Code	Type	Treatment
B0b	ZSM-5	Post-calcined
B1b	Ni-HZSM-5	Post-calcined
B2b	Mo-HZSM-5	Post-calcined
B3b	Co-HZSM-5	Post-calcined
B4b	Fe(2+)-HZSM-5	Post-calcined
B5b	Fe(3+)-HZSM-5	Post-calcined

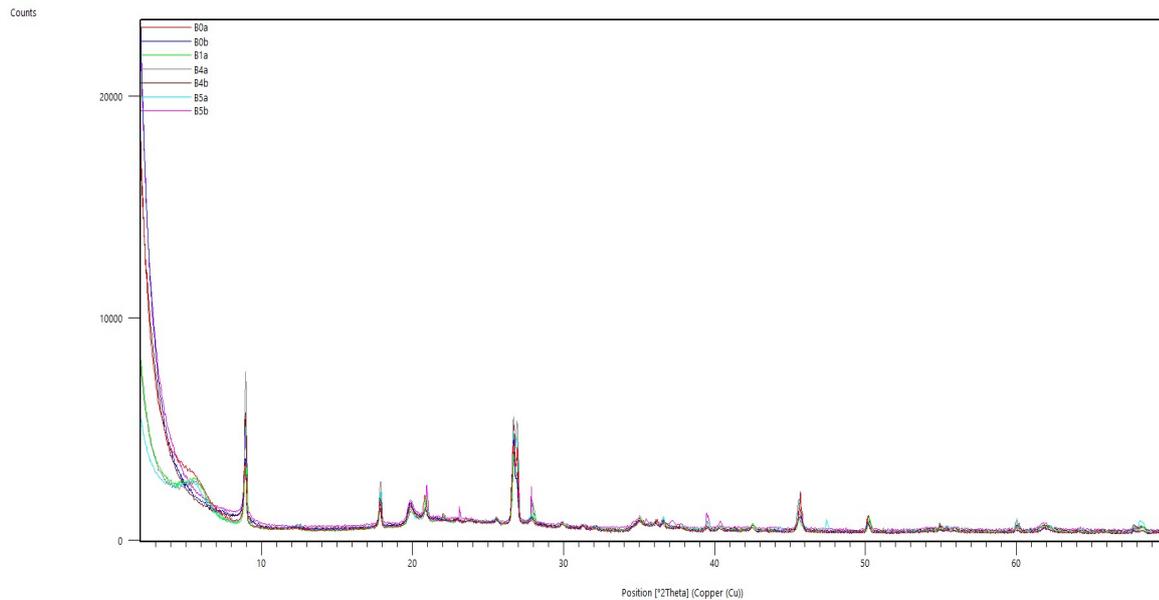


Fig. 1 - X-ray diffraction patterns of some Me-MMT catalysts/*Difragramele unora dintre catalizatorii Me-MMT.*

3.1. Materials characterization

3.1.1. Structural characterization

X-ray diffraction analysis

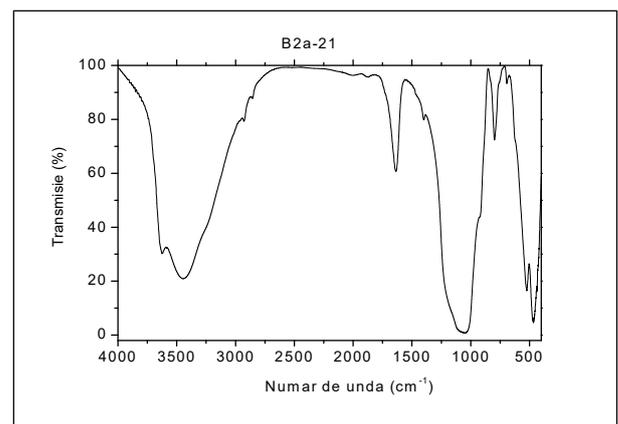
After all samples preparation, the X-ray analysis (XRD) of the resulting potential catalysts was performed in order to identify the crystalline phases and to compare possible effects of the doping transitional metals on the structural network of the montmorillonite (K10).

The reference considered was the as-received K10 montmorillonite before all physical, chemical and heat treatments. All the samples, irrespective of the dopant element, heat treated or not, have shown very 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 of the patterns is obvious. It can be concluded that insertion of the transitional metals within the network of the K10-MMT, as well as the applied heat treatment to simulate catalyst behavior at pyrolysis temperature do not impair upon the structure and its stability. In these circumstances is very likely that doping elements are located in substitutional sites of montmorillonite and, maybe only a small amount within the interstitial sites.

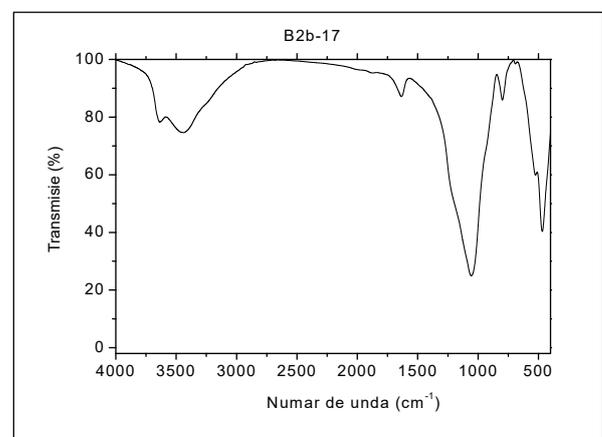
Fourier-transform infrared spectroscopy (FTIR)

As complementary method to X-ray diffraction, FTIR technique can provide additional information in connection to the degree of order/disorder within the network or structural distortions and potential damages.

For pellets preparation 1 mg of sample and 200 mg KBr were homogenized with a magnetic

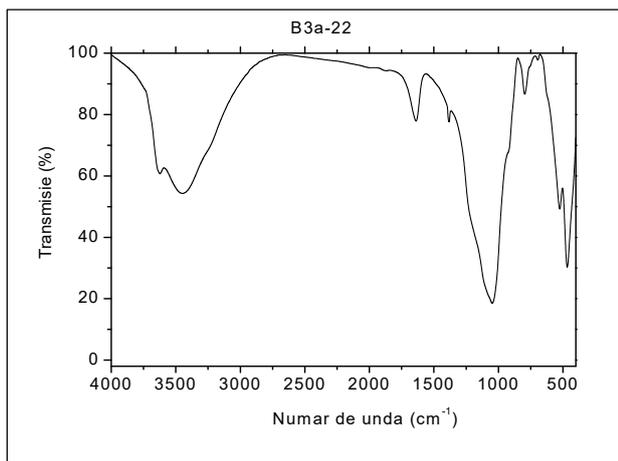


a

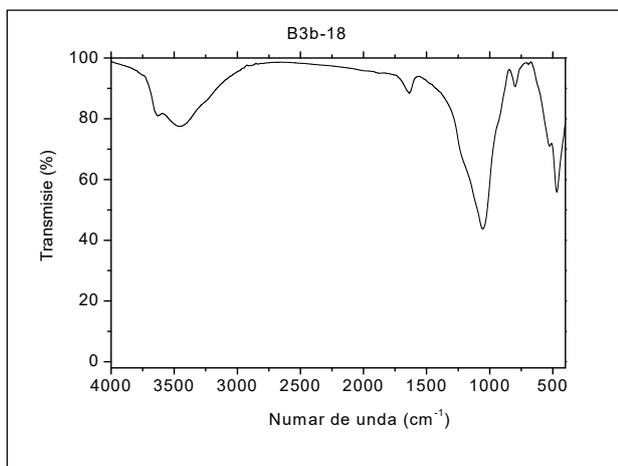


b

Fig. 2 - FTIR Spectrum of Mo-MMT (a) pre-calcined and (b) post calcined/ *Spectrul FTIR al catalizatorului Mo-MMT (a) precalcinată, și (b) post calcinare.*



a



b

Fig.3 - FTIR Spectrum of Co-MMT (a) pre-calcined and (b) post calcined/ Spectrul FTIR al catalizatorului Co-MMT (a) precalcinată, si (b) post calcinare.

homogenizer and then pressed with a force of 1000 N/cm² 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 catalysts

both after synthesis and heat treatment applied. The effects due to dopants presence are missing showing that there is no detectable influence upon the structure of Me-MMT.

For comparison there are given two spectra, Mo-MMT both pre-calcined and post calcined in Figure 2 (a and b), as well as Co-MMT both pre-calcined and post calcined (Figure 3, a and b).

A possible explanation of this behavior is that concentration of doping elements is low enough not to induce any significant deformation or disorder within the initial crystalline structure.

In Table 2 there given the assignment of transmission peaks of all Me-MMT catalysts spectra.

3.1.2. Morphological characterization

Scanning electron microscopy (SEM)

There were analysed from morphological view point all the montmorillonite type materials, doped with transitional metal ions (Ni²⁺, Co²⁺, Mo⁶⁺, Fe²⁺, Fe³⁺) or not, before and after calcination. Comparison between pre-calcined and post-calcined obtained Me-MMT catalysts was performed. To get a very good resolution of the micrographs all samples were covered with a thin layer of gold for SEM analysis.

As a general remark, we have to noticed that a morphological behavioural pattern is to be found for all Me-MMT catalysts both for pre-calcined and post calcined samples.

A first SEM analysis was performed on the purchased ready-made montmorillonite sample (K10). A special morphological structure of the grains can be observed in both the pre-calcined and the calcined sample. Thus, a structure with an "exfoliated" appearance is found due to the stratified structure of montmorillonite. This morphology will be found in practically all the analyzed samples, both pre-calcined and after calcination (see Figs. 4 (a and (b), and Fig. 5 (a) and (b)).

Table 2

		Bands of FTIR spectra										Assignment
Sample B0a	Sample B0b	Sample B1a	Sample B1b	Sample B2a	Sample B2b	Sample B3a	Sample B3b	Sample B4a	Sample B4b	Sample B5a	Sample B5b	
3618	3629	3621	3629	3625	3626	3627	3620	3622	3636	3625	3622	v (O-H)
3443	3447	3448	3447	3447	3445	3441	3467	3455	3435	3455	3450	v (O-H)
2013	-	-				-	-	-	-	2013	-	
1870	-	-		1868	-	-		-	1873	1870	-	
1637	1637	1640	1636	1636	1633	1640	1637	1640	1632	1642	1640	v (O-H)
-	-	1384		1399		1384		-	-	-	-	v (NO) using nitrates
1231 u	1231 u	-						-	-	-	-	
		-						-	1227 u	-	1227	
1050	1057	1046	1057	1050	1057	1064	1054	1047	1054	1046	1054	v (Si-O)
918 u	918 u	909 u				911u		920 u	-	911 u	-	v (Si-O)
798	800	797	799	797	799	797	799	796	799	797	799	v (Si-O)/v (Al-O)
750	-	750				746		750	-	746	-	v (Al-O)
692	689	694	694	693	694	694		686	692	692	694	v (Al-O) in AlOH
670	-	-					668	-	-	-	668	v (Al-O) in AlOH
526	526	522	522	525	525	525	523	522	526	522	525	v (Al-O)
467	467	467	467	467	467	467	467	467	467	467	467	v (Si-O)/v (Al-O)
-	432 u	-		436u				-	-	-	-	

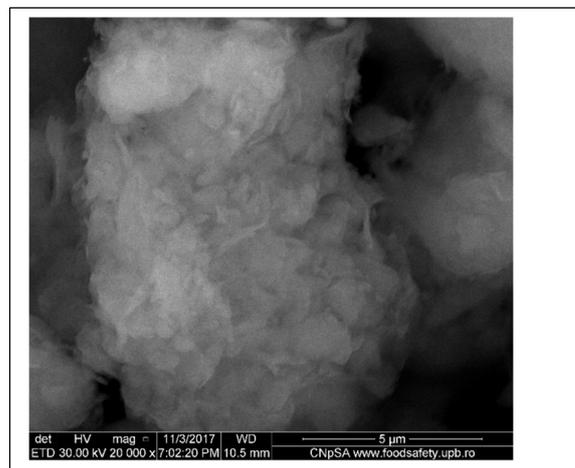
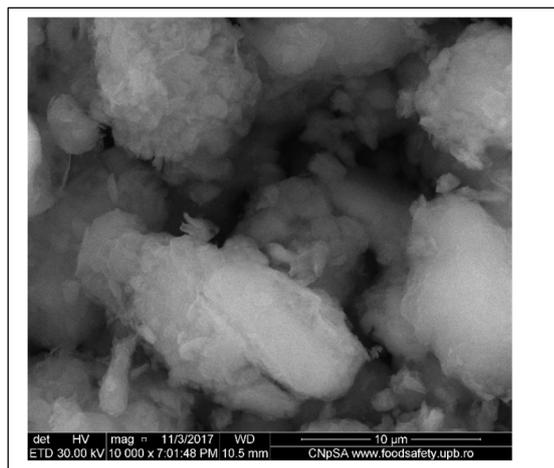


Fig. 4(a) - SEM micrographs of pre-calcined MMT (K10) / *Micrografie SEM a MMT (K10) precalcinată.*

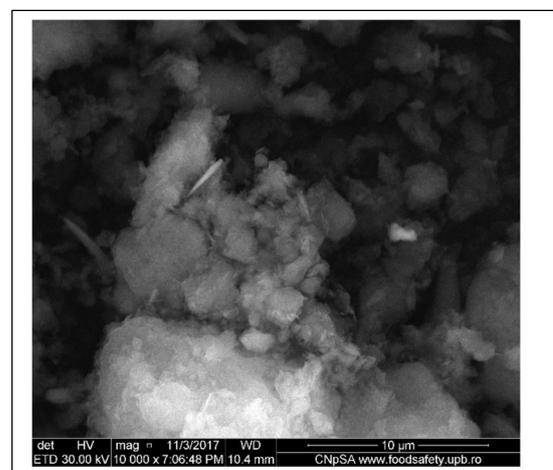
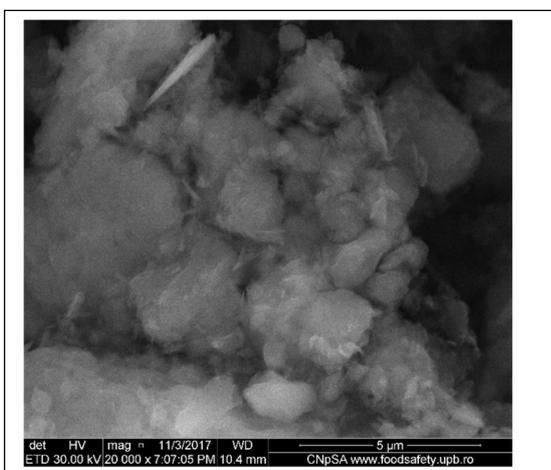


Fig. 4(b) - SEM micrographs of post-calcined MMT (K10) / *Micrografie SEM a MMT (K10) post calcinare.*

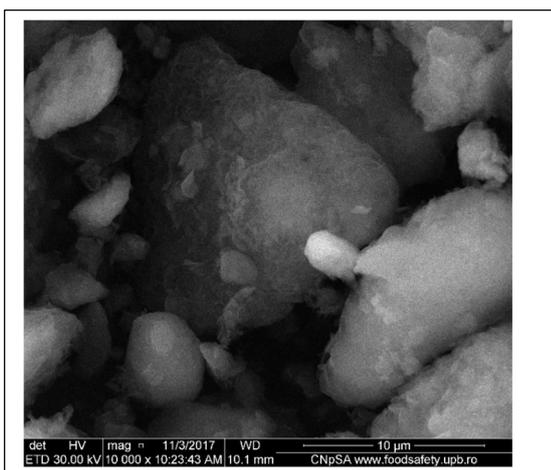


Fig. 5(a) - SEM micrograph of pre-calcined Ni-MMT catalyst / *Micrografie SEM a Ni-MMT precalcinată.*

This structural-morphological pattern is actually recovered for almost all Me-MMT catalysts as obtained and heat treated, with small differences only for the case of Mo-MMT. As a proof of this finding in Figure 5 (a) and (b) there presented the

corresponding micrographs for Ni-MMT sample, pre-calcined and post-calcined, and that of Mo-MMT, as well. The similarities are so obvious, thus supporting that doping and applied heat treatments do not affect the initial structure.

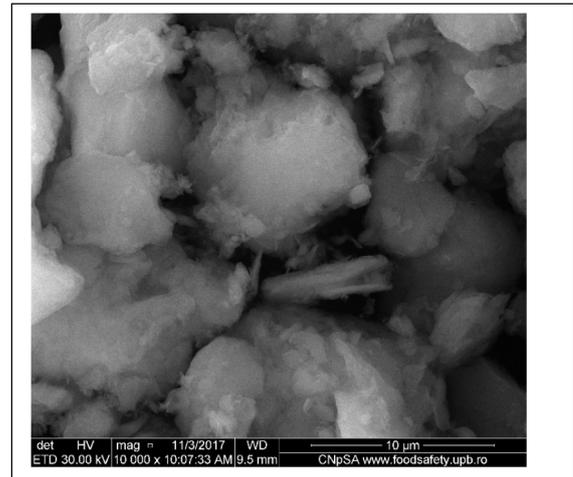
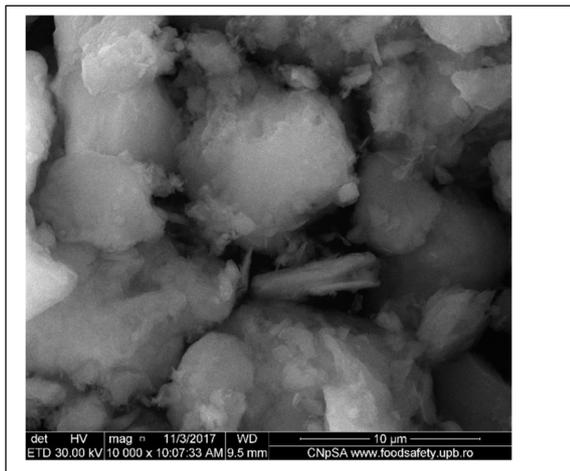


Fig. 5(b) - SEM micrograph of post-calcined Ni-MMT catalyst / *Micrografie SEM a Ni-MMT post calcinată.*

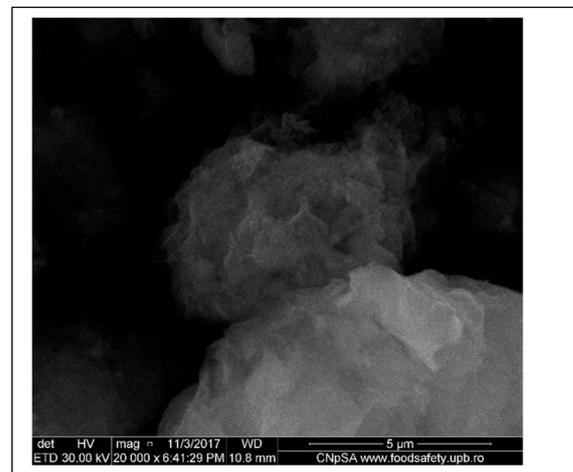
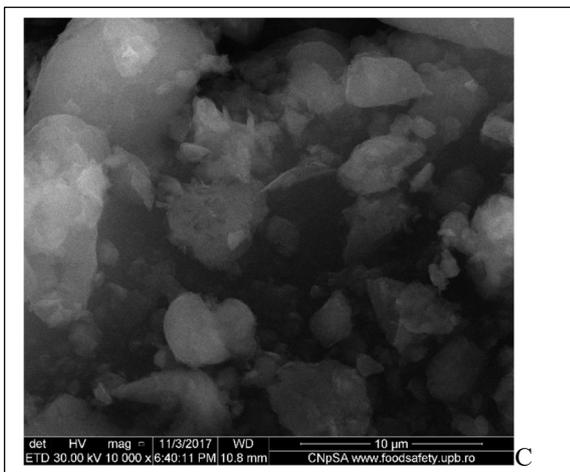


Fig. 6(a) - SEM micrograph of pre-calcined Mo-MMT catalyst / *Micrografie SEM a Mo-MMT precalcinată.*

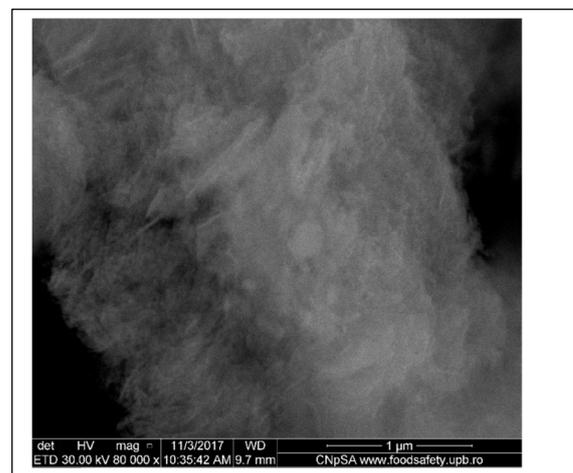
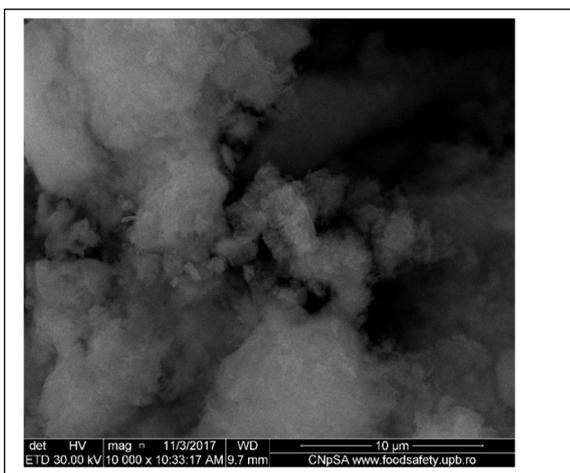


Fig. 6(b) - SEM micrograph of post-calcined Mo-MMT catalyst / *Micrografie SEM a Mo-MMT post calcinată.*

In the case of samples doped with molybdenum, an interesting phenomenon appears. If the pre-calcined sample has a similar appearance to those found in previous cases, from a morphological and microtextural point of view, the calcined sample has an exfoliated-loose

appearance which indicates a process of expansion of the inter-layers area, probably due to the elimination of hydroxyl groups in the structure of montmorillonite. The following Figures (6, a and b) show the SEM micrographs for the two situations.

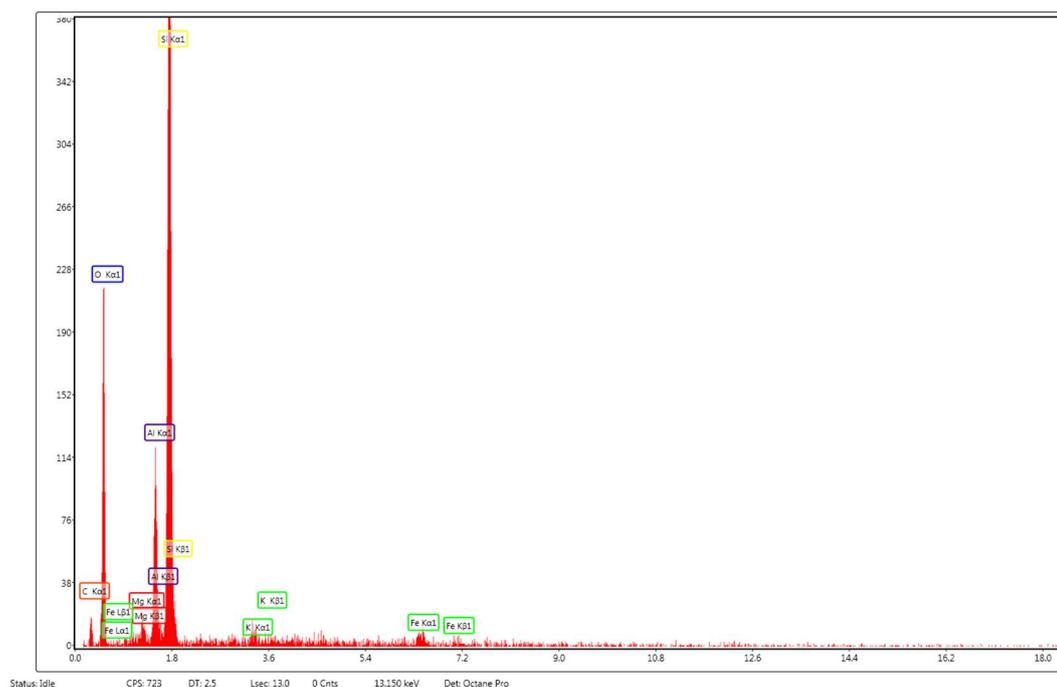


Fig. 7(a) - EDAX spectrum of pre-calcined MMT (K10) sample / *Spectrul EDAX a catalizatorului MMT (K10) precalcinat*



Fig. 7(b) - EDAX spectrum of post-calcined MMT (K10) sample / *Spectrul EDAX a catalizatorului MMT (K10) postcalcinat*

Energy dispersive X-ray spectroscopy (EDAX)

If morphological and structural behavior as proved by means of X-ray, FTIR and SEM analyses is essentially similar for all Me-MMT catalysts, the elemental compositional characteristics were studied based on EDAX spectroscopy.

The elemental analysis of this MMT-stock sample (K10) highlights the normal presence of aluminum, silica, oxygen, to which are added iron, magnesium and potassium elements found in the

structure of montmorillonite especially in the positions between the layered structures of this type of clay. The EDAX spectra for pre-calcined and post calcined are presented above.

Their similarity is obvious, which leads to the conclusion that the heat treatment does not affect the chemical composition of montmorillonite. Moreover, this conclusion remains valid even in the case of doped MMT samples in full agreement with XRD and FTIR determinations.

From the point of view of the elemental analysis for these samples doped (e.g. with Mo), we find exactly the same observations as in the previous cases with the conclusion that the heat treatment does not affect from a compositional point of view but only texturally and morphologically.

The two figures below show the EDAX spectra that support the observations made. The same

types of ions characteristic of montmorillonite are highlighted, including the dopant Mo (figs. 8 a and b).

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-MMT catalysts.

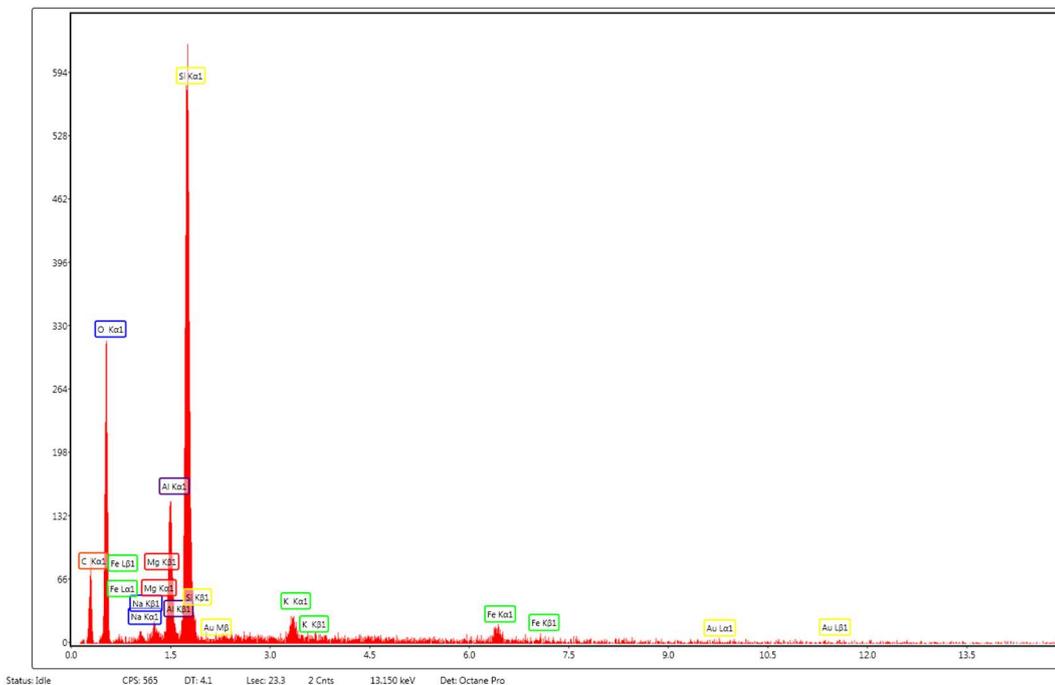


Fig. 8(a) - EDAX spectrum of pre-calcined Mo-MMT catalyst/ *Spectrul EDAX a catalizatorului Mo-MMT precalcinață*

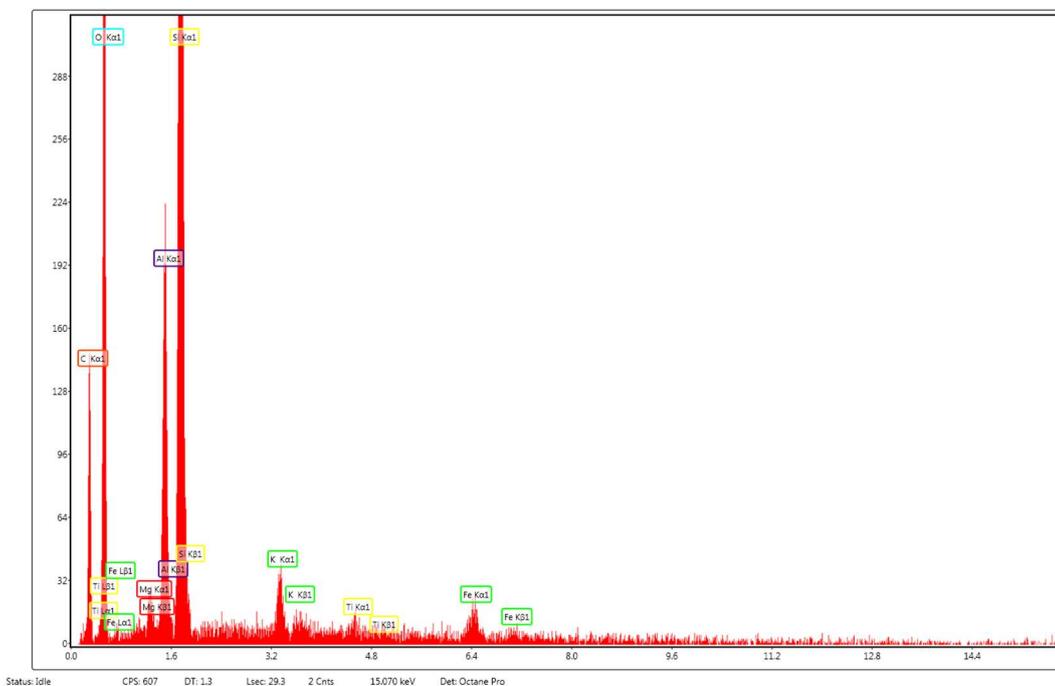


Fig. 8(b) - EDAX spectrum of post-calcined Mo-MMT catalyst/ *Spectrul EDAX a catalizatorului Mo-MMT postcalcinat*

4. Conclusions

The main target of present work was to study the synthesis and structural characterization of transitional metals doped-montmorillonite (Me-MMT) type catalysts, together with a thermal simulation through applied heat treatment, of their potential behaviour in pyrolysis and gasification process of different vegetal wastes.

The syntheses of Me-MMT 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.

Structural, morphological and chemical stability characterization for the obtained potential catalysts were performed using specific methods as described in the paper. A post-calcination heat treatment was subjected to all doped montmorillonites 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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