

Preparation and application of metal loaded ZSM-5 and γ -zeolite catalysts for thermo-catalytic pyrolysis of real end of life vehicle plastics waste

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Abstract

In this work synthetic zeolite catalysts were modified by metal loading and used for real end of life vehicle plastic waste pyrolysis. ZSM-5 and γ -zeolite catalysts were loaded by Ce^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , H^+ , Mg^{2+} , Ni^{2+} , Sn^{2+} and Zn^{2+} and the catalytic effects of both parent and metal loaded catalysts were tested by thermogravimetric method. The catalysts morphology and other properties were followed by N_2 adsorption/desorption isotherms, Fourier transformed infrared spectroscopy, Scanning Electron Microscopy and energy dispersive x-ray fluorescent spectroscopy. Significant difference in micropore, mesopore and macropore surface area, and average pore diameter was concluded. In general, the surface areas could be decreased by metal loading onto the catalyst surface. Parent γ -zeolite had larger surface areas than that of parent ZSM-5 catalyst. Based on EDXRF analysis, catalysts were loaded by 8-10% metals. Regarding grain size, in general γ -zeolite based catalysts had smaller grains and the distribution was also narrower, than ZSM-5 based catalysts. The Si/Al ratio was 17.11-21.75 in case of ZSM-5 catalysts and 2.04-2.91 regarding γ -zeolite catalyst. Based on first order kinetic approach, the reaction kinetic parameters were also calculated and evaluated. Waste end-of life vehicle (ELV) started to decompose at 426 °C ($T_{5\%}$) and finished at 525 °C ($T_{95\%}$). Catalysts can decrease the activation energies of decomposition. Same order of the activation energy decreasing of both ZSM-5 and γ -zeolite based catalysts was found: $\text{Cu} < \text{Ce} < \text{Mg} < \text{Ni} < \text{Fe(III)} < \text{Fe(II)} < \text{Zn} < \text{Sn}$, however, γ -zeolite based catalysts had advanced properties in activation energy decreasing than ZSM-5 based.

Keywords: metal loaded catalysts, ZSM-5, γ -zeolite, weight loss, activation energy

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1. Introduction

Among the different ways for waste plastic utilizations, pyrolysis looks attractive and environmentally friendly possibility for long term sustainable waste utilization. Furthermore, waste polymers could be converting into valuable feed-stocks by this way. It is also known, that the so called chemical recycling has numerous impacts and positive effects to the carbon footprint. Either energy or CO₂ emission could be saved by pyrolysis. The effects of the pyrolysis conditions (temperature, catalyst, raw material, reactor construction, etc.) to the product properties are widely investigated. Catalysts can support the cracking of C-C bonds, which led to increasing in both gas and pyrolysis oil yields and they affect the composition of pyrolyzed products, too. Regarding waste plastic pyrolysis, different synthetic zeolites are efficiently used as catalysts; e.g. ZSM-5, γ -zeolite, β -zeolite, mordenite, etc. [1-5]. They have high surface areas; advanced pore structure, high acidity and advanced Si/Al ratio to accelerate the decomposition reactions. It is also known, that the three dimensional structure of zeolite catalysts built up by SiO₄ and AlO₄ tetrahedral via common oxygen atoms [6]. The ratio of Al³⁺ and Si⁴⁺ ions, water and alkaline ions in the framework and pore structure are key regarding the catalytic effect. Active sites are located in pores; dominantly in internal surface. Catalytic decomposition occurs by ionic mechanism and as it was demonstrated; catalysts can decrease the activation energy of initiation reaction step.

The catalytic effect of ZSM-5 (MFI-type, 10 membered rings, built from pentasil unit) and γ -zeolite (FAU-type, 12 membered rings, built from sodalite unit) catalysts is extensively studied. They can increase the yield of valuable products, isomerize the main carbon frame, cracking the heavy compounds and converted them into aromatics. The catalytic performance have been investigated in different type of reactors, e.g. fluidised beds [7-9], fixed beds [10-15], spouted beds [16-19], screw kilns [20], or different reactor configurations (in situ, where the catalyst is mixed with the raw materials [21] or in line, where the catalytic bed is independent [14]) as it has been summarized by G. Lopez et al [5].. Each reactor type has advantageous and disadvantageous. For example fixed bed reactor has low investment cost, fluidised bed types allow for catalyst circulation, spouted bed types provide short residence time and very high specific capacity, furthermore screw kiln types afford good control of solid residence time. Fix beds and screw kilns have simple design, construction and no limitation on particle size, while fluidized and spouted beds have high heat transfer rate, good gas-solid contact and efficient contact with catalyst in situ. The significant disadvantages of fixed bed reactors are the poor contact with catalyst in situ, poor gas-solid contact and low specific capacity, fluidized bed reactors have high investment cost and defluidization problems. Regarding spouted bed reactor the catalyst circulation is difficult, while the screw kilns have low heat efficiency and high maintenance cost [5].

The change in catalyst framework, channels or quality and quantity of non-framework ions affected both the catalyst activity and selectivity. The effect of catalyst surface areas, pore structure, Si/Al ratio or acidity to the properties of pyrolyzed products is widely investigated. It was found, that higher surface areas, and acidity favour to the volatile yield increasing; in general, higher microporous surface area increases especially the gas yields, however high meso- and macroporous surface area led to increasing in pyrolysis oil yields [1-3,6,22,23]. Y-zeolite catalyst has high activity in increasing of toluene, xylenes and long alkyl chain substituted benzene [24]. ZSM-5 was added to the y-zeolite structure and efficiently used for increasing in pyrolysis oil yield and decreasing in both coke and gas yield by Ofei D. Mante et al. [25].

Recently more attention took towards the metal loading of typical cracking catalysts, such as ZSM-5 for waste plastic, biomass or even lignite pyrolysis [26-29]. Alkali metal ions in catalysts pore channel can be effectively modify by wet impregnation or ion-exchange procedure [27]. The transition metal modified zeolite catalysts are typically used for cyclization, aromatization, reforming or steam-reforming reactions in the presence of water/steam led to hydrogen production. Those reactions require elevated temperature and resulting increased hydrogen concentration, yields of aromatic compounds, etc. For wet impregnation 150-170 °C temperature are used and metals are represented up to 10% in catalyst structure. Comparing catalysts prepared by wet impregnation and ion-exchange methods, lower selectivity for aromatization reactions was concluded using ion-exchange method in case of Co, Ni, Mo and Ga loaded ZSM-5 catalysts [27]. E.F. Iliopoulou et al. demonstrated that the product quality increased with increasing Ni and Co content of ZSM-5 catalyst, however, Ni modified catalyst showed higher activity in gas yield increasing than Co modified ZSM-5 catalyst [29]. Due to the aromatization and deoxygenation, Ni/HZSM-5 exhibited advanced property for in-situ pyrolysis oil upgrading obtained from lignite, too [28]. Advanced property of Zn/ZSM-5 catalyst with 0.5-5.0% zinc content was also reported by Lu Wang et al. using microwave pyrolysis reactor [30]. More hydrogen and aromatic compounds and less coke were obtained by the using of Zn/ZSM-5 catalyst compared to non-metal loaded ZSM-5. Owing to the partial blockage in ZSM-5 structure by MgO and ZnO, reduced catalytic effect was found in case of biomass pyrolysis at 500° by J. Feroso et al. [31].

The goal of this work was the preparation and application of metal loaded ZSM-5 and y-zeolite catalysts using Ce^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , Ni^{2+} , Sn^{2+} and Zn^{2+} . Catalysts were added in 5% concentration to real ELV plastic waste for pyrolysis and the catalytic effects were also followed by thermogravimetric apparatus via the apparent reaction kinetic parameters, based on first order kinetic approach. As it was before mentioned both ZSM-5 and y-zeolite are widely used catalyst for waste pyrolysis using different reactor configurations.

Transition metals in catalyst structure, or metal oxides combined with ZSM-5 and γ -zeolite catalysts can affect mainly the composition of products and had less effect to the yields of volatiles. Our current work is dedicated to the catalyst selection for a further work, when the effect of selected metal loaded catalysts will be used for real waste pyrolysis in pilot scale process focussing to the in-situ pyrolysis product upgrading and volatile yield increasing compared to catalyst free pyrolysis.

2. Experimental

2.1. Materials

2.1.1. Waste plastics

Owing to the strict regulation for waste polymer recycling, real ELV plastic waste was used as raw materials (engine containers, bumper, fuel tank, wheel rims, etc.) containing 41% HDPE, 42% PP and 17% LDPE. Firstly, plastic wastes had been shredded and milled into 2-4mm particles and then the grain size was further reduced to 0.01-0.1mm size by cryogenic mill. The moisture content of raw material was 1.1%, which was calculated based on its weight loss. Sample was treated in a drying cabinet at 110 °C during to constant weight of sample. According to proximate analysis raw material had 5.2% ash content, 0.4% volatiles and 94.4% combustible. Ash content was measured at 850 °C in air atmosphere, while the volatiles based on the weight loss at controlled conditions corrected with moisture content using electric heated furnace. Based on ultimate analysis, the carbon and hydrogen content was 85.5 and 14.5%. During ultimate analysis, ELV waste was heated in a quartz tube under controlled conditions in oxygen atmosphere. The carbon content of raw material was calculated based on the carbon oxides formed in oxidation reactions.

2.1.2. Catalysts and their properties

Catalysts were prepared as following: ZSM-5 and γ -zeolite catalysts were continuously stirred in 1M dissolution of NH_4NO_3 , $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{SnSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 80 °C. Then the solid and liquid phase were separated by filtration and catalysts were dried for 10 hours at 110 °C, and then conditioned at 600°C for 5 hours in air.

The catalyst morphology was analysed by N_2 adsorption/desorption isotherms using Micromeritics ASAP 2000-type instrument (ASAP 2000 operational program V1.03). Firstly 1 g sample of catalyst was previously outgassed in vacuum at 160 °C. Surface areas were determined by the BET (Brunauer-Emmett-Teller) method from the nitrogen adsorption isotherm. The pore volume, pore volume distribution, pore size, pore size

distribution, average pore size and volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) model.

The main properties of the catalysts are summarized in Table 1. In general, the pore size obtained from the BJH analysis showed similarities with that of obtained from BET analysis in case of ZSM-5 catalyst. However, significant differences were demonstrated between the BET and BJH surfaces regarding modified γ -zeolite catalysts. As it is known, that BET surface area refers to the multilayer coverage, while BJH surface area corresponds to the mesopores and small macropores surface areas.

Table 1
Main properties of catalysts

	S_{BET} m^2/g	S_{BJH} m^2/g^*	Pore volume $V_{1.7-300}$ $\text{nm}, \text{cm}^3/\text{g}$	S_{micro} m^2/g	V_{micro} cm^3/g	Range, μm	Average, μm	D_{av} , nm^*	Si/Al	Elements
ZSM-5	355	90	0.085	221	0.104	0.3-17.5	3.16	1.74	21.75	-
Ce/ZSM-5	285	92	0.083	160	0.075	0.4-17.4	3.09	1.79	20.92	Ce (9.7%)
Cu/ZSM-5	298	92	0.086	164	0.077	0.3-16.8	3.15	1.80	17.11	Cu (9.3%)
Fe(II)/ZSM-5	355	112	0.104	191	0.089	0.4-17.7	3.19	1.81	18.05	Fe (8.5%)
Fe(III)/ZSM-5	351	111	0.102	188	0.087	0.4-17.2	3.22	1.80	17.87	Fe (8.9%)
H/ZSM-5	356	112	0.103	188	0.088	0.3-16.5	3.06	1.81	20.35	-
Mg/ZSM-5	345	109	0.100	194	0.091	0.4-17.3	3.11	1.80	17.29	Mg (8.9%)
Ni/ZSM-5	320	102	0.093	177	0.083	0.3-17.6	3.18	1.81	17.53	Ni (8.7%)
Sn/ZSM-5	319	105	0.109	166	0.077	0.3-18.1	3.35	1.92	18.64	Sn (9.8%)
Zn/ZSM-5	268	73	0.065	158	0.074	0.3-17.2	3.20	1.72	17.98	Zn (9.1%)
γ-zeolite	634	32	0.036	582	0.276	0.1-6.4	1.45	1.49	2.91	-
Ce/γ-zeolite	583	34	0.034	505	0.232	0.1-6.7	1.44	1.51	2.08	(9.9%)
Cu/γ-zeolite	604	29	0.033	559	0.265	0.1-6.3	1.27	1.50	2.04	(10.1%)
Fe (II)/γ-zeolite	514	32	0.036	454	0.215	0.2-7.2	1.35	1.52	2.71	(9.5%)
Fe (III)/γ-zeolite	540	35	0.034	461	0.203	0.1-6.8	1.40	1.51	2.50	(9.9%)
H/Y-zeolite	619	26	0.030	576	0.274	0.1-7.1	1.44	1.48	2.88	-
Mg/γ-zeolite	654	27	0.031	610	0.290	0.2-6.6	1.38	1.48	2.28	(9.4%)
Ni/γ-zeolite	621	25	0.031	559	0.274	0.1-7.0	1.41	1.43	2.44	(10.2%)
Sn/γ-zeolite	455	57	0.031	506	0.250	0.1-8.8	1.83	1.71	2.75	(9.5%)
Zn/γ-zeolite	628	27	0.032	583	0.278	0.2-7.1	1.24	1.49	2.19	(9.8%)

As it is well shown, the surface areas decreased by metal loading (BET, BJH and micropore surface areas), which was confirmed by others. E.F. Iliopoulou et al. demonstrated that the BET area slightly decreased as function of metal content of catalysts up to 5%, however owing to catalyst micropores blockage, significant BET surface decreasing was found between 5% and 10% metal content [12]. Similar result was concluded by S.

Vitolo et al. The blockage refers better metal incorporation into catalyst pore [15]. It is important observation, that the BET surface decreased by metal loading, however, the BJH surface can increase in case of Fe(II), Fe(III), H, Mg, Ni and Sn loaded ZSM-5 catalysts. Comparing ZSM-5 and γ -zeolite catalysts, it can be said, that γ -zeolite based catalysts had higher BET and BJH surface, however, lower micropore surface area than ZSM-5 based catalysts. It means that γ -zeolite and modified γ -zeolite catalysts had dominant mesopore (2–50 nm) and macropore (50–100 nm) surface area, while ZSM-5 based catalysts had comparable micro and meso- or macropore surface area.

The grain size distributions of catalysts were investigated by Fritsch Analisette 22 instrument, while the morphology of catalysts was followed by SEM method (Phillips XL30 ESEM instrument). Results show that modified ZSM-5 catalysts comprised larger grains than γ -zeolite based (Table 1, Figures 3 and 4). As Table 1 shows, the average grain size of ZSM-5 based catalysts changed between 3.06 μm (H/ZSM-5) and 3.35 μm (Sn/ZSM-5), however that of were between 1.24 μm (Zn/ γ -zeolite) and 1.83 μm (Sn/ γ -zeolite). According to the grain size distribution, ZSM-5 catalysts had wider range than that of γ -zeolite based. SEM micrographs (Figures 3 and 4) well demonstrate, the catalyst agglomerates, because the individual grain size of catalysts was considerable less than 1-2 μm . In general, catalysts powder agglomerates can be formed by interconnections of individual grains. ZSM-5 based catalyst agglomeration contained ball-like catalysts grain; while γ -zeolite based catalysts agglomerate had rather smaller sized, sharp, cube-like catalyst grains. It is also clear, that metal loading of catalysts could not result significant change in their morphology, each ZSM-5 and all γ -zeolite based catalyst had very similar catalysts grains.

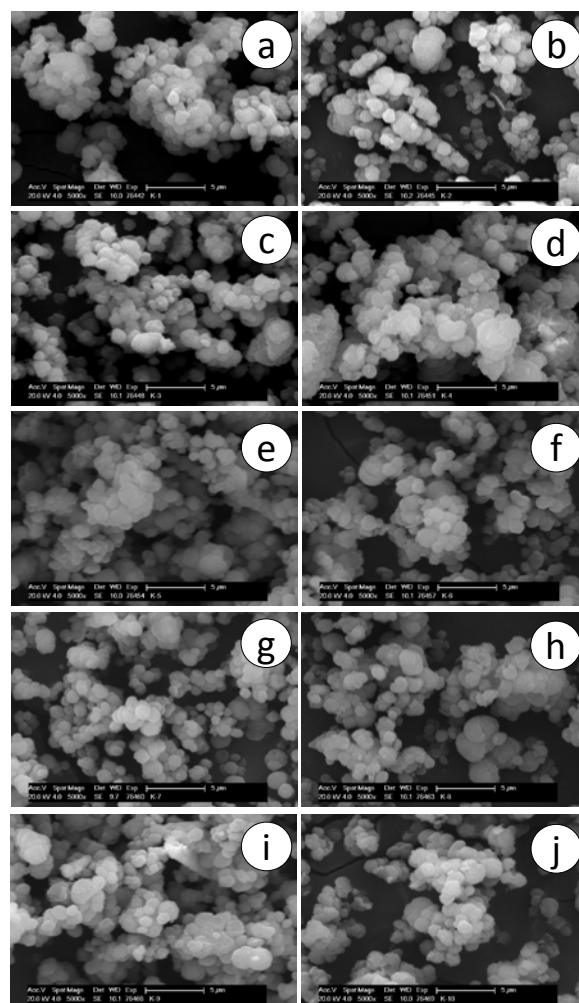


Figure 3
SEM micrograph of ZSM based catalysts

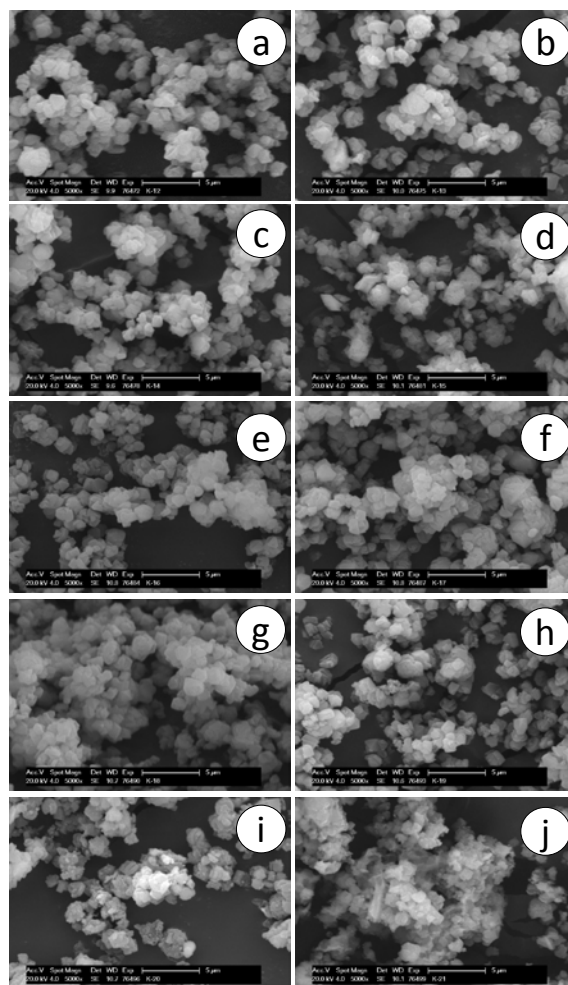


Figure 4
SEM micrograph of γ -zeolite based catalysts

Energy dispersive x-ray fluorescent spectroscopy was used for determination of elemental composition of catalysts (PHILIPS MiniPal PW 4025/02 non-polarized EDXRF spectrometer (Philips Co., Alamenno, Netherlands), powered by PW 4051 MiniPal/MiniMate Software V 2.0A). The metal content and Si/Al ratio of metal loaded catalyst surface is also summarized in Table 1. ZSM-5 catalyst contained 8.5-9.8% metals, while γ -zeolite.4-10.2%. ZSM-5 catalysts had higher Si/Al ratio (17.11-21.75), than γ -zeolite (2.04-2.91). However, in case of both ZSM-5 and γ -zeolite based catalysts, the metal loading can decrease the Si/Al ratio.

The framework of zeolite catalysts shows infrared activity in mid-range; therefore the structure of ZSM-5 and γ -zeolite catalysts was also followed via their infrared spectra between 400 and 4000 cm^{-1} . The synthesized catalysts cause significant infrared band around 800 cm^{-1} , 1100 cm^{-1} , which correspond to the symmetric and asymmetric stretching vibration of internal tetrahedral (Figure 5).

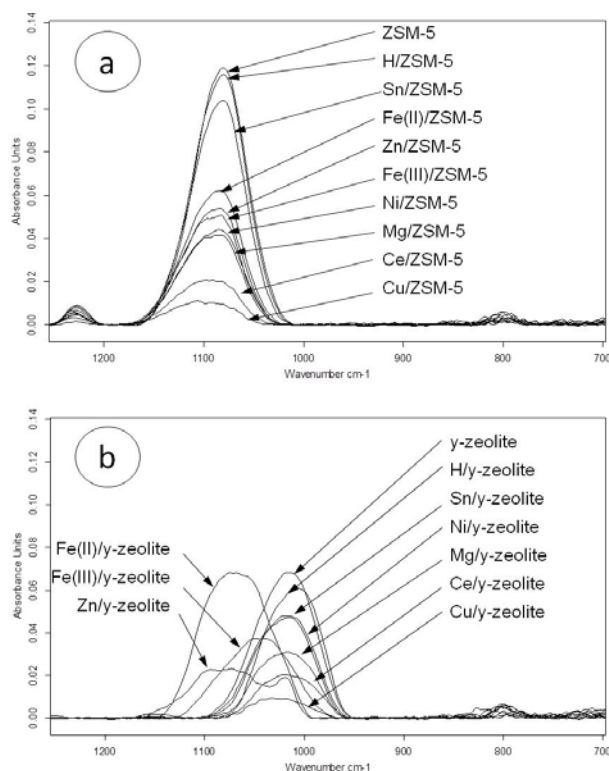


Figure 5
FTIR spectra of catalysts ((a)-ZSM-5 based, (b)-y-zeolite based)

Fact, that the catalyst acidity is proportional to Al^{3+} content, however, the strength of the active acid sites increases with increasing Si/Al or decreasing Al^{3+} concentration. FTIR spectra well shows, that parent ZSM-5 and y-zeolite catalysts had the most intensive adsorption bands at 1100cm^{-1} , which can be decreased by the metal loading. Regarding the ZSM-5 based catalysts the order of H^+ , Sn^{2+} , Fe^{2+} , Zn^{2+} , Fe^{3+} , Ni^{2+} , Mg^{2+} , Ce^{2+} and Cu^{2+} was concluded, which is similar as it was found in case of Si/Al ratio by x-ray technique. The order of infrared band intensity decreasing was also same using y-zeolite based catalysts. It is also know, that the position of infrared band can shifted by the change in catalysts framework structure. Modified ZSM-5 catalysts had similar zeolite frame, than parent ZSM-5, however, owing to the modification in metal loaded y-zeolite catalysts structure compare to parent y-zeolite, the infrared band around 1100cm^{-1} is shifted.

2.2. Method and theory

The apparent kinetic parameters of the decomposition and the effects of the modified ZSM-5 and y-zeolite catalysts during the pyrolysis of real waste ELV plastics were investigated using TGA analysis (MOM DERIVATOGRAPH Q-1500 D type instrument). Firstly 110mg of ELV sample and 10% of catalysts were weighted in the sample holder and placed in the instrument. Then $20\text{ }^{\circ}\text{C}/\text{min}$ heating rate and $40\text{ml}/\text{min}$ nitrogen flow was used for analysis. The final temperature was $800\text{ }^{\circ}\text{C}$.

The activation energy and pre-exponential factor was calculated by first order kinetic approach [16-18]. The weight loss fraction of ELV sample was calculated by the following equation:

$$x = \frac{m_i - m_t}{m_i - m_f} \cdot 100$$

where “ m_i ”, “ m_t ” and “ m_f ” are the initial weight of sample, sample weight at “ t ” time and final weight of sample, respectively. As it is also known, that the weight loss is the function of activation energy [15-17]:

$$\frac{dx}{dt} = A \cdot e^{\left(-\frac{E}{RT}\right)(1-x)}$$

where “ A ” is the pre-exponential factor, “ E ” is the activation energy, “ T ” is the temperature, “ t ” is the time for reaction and “ R ” is the universal gas constant.

3. Result and discussion

Based on both TG and DTG curves, the main decomposition step occurs in the temperature range of 430-500°C, which were affected by catalysts (Figures 6 and 7). The solid residue yields were 6.7% without catalysts, however it was between 16.7-17.3% in thermo-catalytic pyrolysis. Catalyst remain in the solid residue was the cause for the higher values of residues in thermo-catalytic pyrolysis. Residue contains mainly reinforcements (e.g. glass fibre) from raw materials in case of non-catalytic pyrolysis. Table 2 shows the apparent results of ELV thermal and thermo-catalytic pyrolysis; $T_{5\%}$, T_{\max} and $T_{95\%}$ temperatures. Without catalyst, 5% of the initial weight was decomposed till 426 °C. Then the decomposition suddenly increased and reached the maximum value of “ dx/dt ” at 488 °C and rapidly decreased after 488°C. The 95% weight loss of the initial sample occurred up to 525 °C without catalyst. It is clear, that catalysts can promote the decomposition reactions, therefore temperatures shifted towards lower values. The peak maximums of decomposition rate are between 438-473 °C in case of thermo-catalytic pyrolysis. Parent ZSM-5 and γ -zeolite catalysts can shift the value of T_{\max} to 465 and 460 °C. Real waste ELV begins to decompose ($T_{5\%}$) at 349 °C and finished ($T_{95\%}$) at 510°C using ZSM-5 catalyst, on the other hand those values are 336 °C and 478 °C over γ -zeolite catalyst.

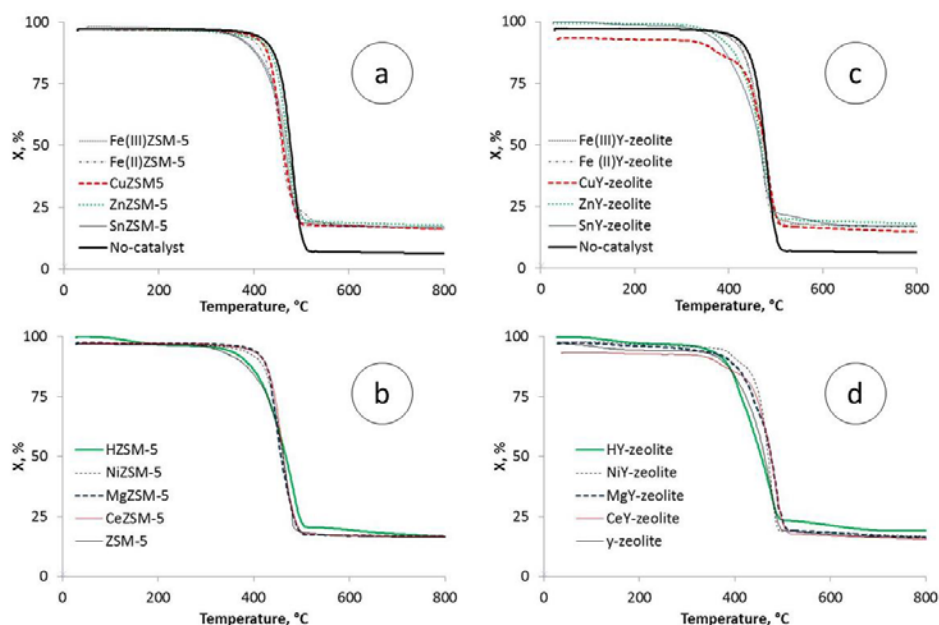


Figure 6
Weight loss curves of ELV and ELV with ZSM-5 (a,b) and y-zeolite (c,d) based catalysts

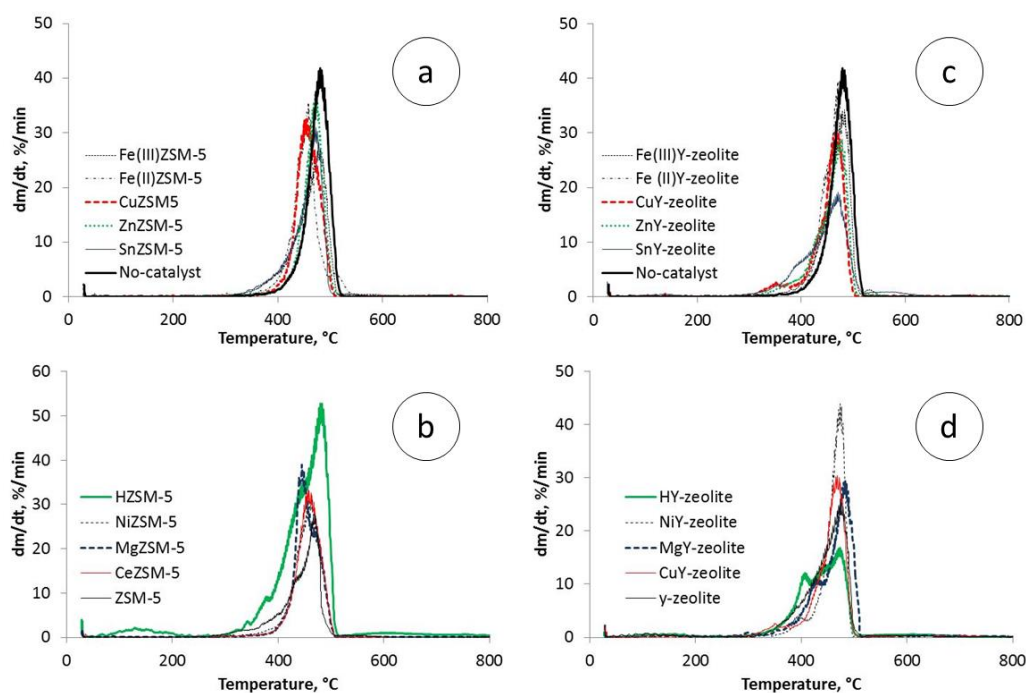


Figure 7
DTG curves of ELV and ELV with ZSM-5 (a,b) and y-zeolite (c,d) based catalysts

Regarding modified ZSM-5 catalysts, Ni/ZSM-5 resulted the lowest $T_{5\%}$ value (349 °C), while Fe(II)/ZSM-5 the lowest maximum value (449°C) and $T_{95\%}$ (505°C). On the other hand, 5% weight loss is occurred at 408 °C using Ce/ZSM-5 and Zn/ZSM-5 modified catalysts. Mg/ZSM-5 catalyst has a slight effect to the maximum of dx/dt , because 471 °C of T_{max} is calculated. Data in Table 1 demonstrates that Zn/ZSM-5, Ce/ZSM-5 and Cu/ZSM-5 have the smallest BET surface area; less than 300m²/g. Zn/ZSM-5 and Cu/ZSM-5

catalysts have low Si/Al ratio, however it was the highest in case of Ce/ZSM-5. These three catalysts can decrease only slightly the initial temperature of pyrolysis ($T_{5\%}$); 408, 408 and 405 °C, respectively. ZSM-5, H/ZSM-5 and Fe(II)/ZSM-5 catalysts have the highest BET surface area, with 355, 356 and 354 m²/g values. Results in Table 2 well show, that the use of Fe(II)/ZSM-5, ZSM-5 and H/ZSM-5 catalysts has the most notable effect to the decomposition, decreasing to 449, 450 and 452 °C, respectively. Regarding Si/Al ratio, ZSM-5 and H/ZSM-5 catalysts had high values (>20), however Fe(II)/ZSM-5 had relatively low value (18.05).

Table 2
Apparent results for ELV thermal and thermo-catalytic pyrolysis ($T_{5\%}$, T_{max} and $T_{95\%}$ temperatures)

	$T_{5\%}$, °C	T_{max} , °C	$T_{95\%}$, °C
No-catalyst	426	488	525
ZSM-5	349	450	510
H/ZSM-5	360	452	509
Ce/ZSM-5	408	454	514
Cu/ZSM-5	405	458	519
Fe(II)/ZSM-5	398	449	505
Fe(III)/ZSM-5	391	458	510
Mg/ZSM-5	362	471	510
Ni/ZSM-5	349	452	520
Sn/ZSM-5	374	464	511
Zn/ZSM-5	408	467	518
y-zeolite	336	430	519
H/y-zeolite	322	428	520
Ce/y-zeolite	388	459	510
Cu/y-zeolite	402	457	508
Fe(II)/y-zeolite	322	473	514
Fe(III)/y-zeolite	406	474	507
Mg/y-zeolite	310	458	519
Ni/y-zeolite	408	464	517
Sn/y-zeolite	349	470	510
Zn/y-zeolite	381	473	505

It is important result, that the surface area has more effect to the pyrolysis reactions than acidity in case of Ce/ZSM-5, because that catalyst can decrease the T_{max} temperature (454 °C) significantly; however, it has relatively low surface area, with high Si/Al ratio. Regarding $T_{95\%}$ temperature, similar result was concluded. Whereas, catalysts with high BET and BJT surface areas, show high activity decreasing in $T_{95\%}$; e.g. ZSM-5, HZSM-5 and Fe(II)/ZSM-5, while catalyst with low surface areas result less effect to the end section of weight loss curves (e.g. Zn/ZSM-5, Ce/ZSM-5 and Cu/ZSM-5). Comparing the catalytic effect of Fe(II)/ZSM-5 and

Fe(III)/ZSM-5, only slight different can be concluded. The decomposition begins later (at 398 °C) using Fe(II)/ZSM-5 catalyst, but the maximum of decomposition rate and $T_{95\%}$ occur at lower temperatures, that in case of Fe(III)/ZSM-5 catalyst. Both catalysts have similar surface areas (355m²/g and 351m²/g BET surface) and Si/Al ratio (18.05 and 17.87).

Glancing the metal loaded γ -zeolite catalysts, the decomposition begin ($T_{5\%}$) at 322 °C using H/ γ -zeolite and Fe(II)/ γ -zeolite, however higher temperatures belong to 5% decomposition are concluded in case of Ce/ γ -zeolite (388 °C) or Zn/ γ -zeolite (381 °C). It is important observation, that $T_{5\%}$ temperatures of 310 °C can be measured using Mg/ γ -zeolite catalyst with high surface area (S_{BET} =654m²/g), however the decomposition rate maximum is not the lowest (458 °C). The cause for that phenomenon is the low value of Si/Al ratio. H/ γ -zeolite and Fe(II)/ γ -zeolite catalysts had 2.88 and 2.71 Si/Al ratio, while Mg/ γ -zeolite had only 2.28. Regarding the decomposition ratio maximum, the highest activity in reaction ratio increasing of γ -zeolite and H/ γ -zeolite catalysts are concluded (430 and 428 °C). Those catalysts had the highest BET surface area and Si/Al ratio. Fe(II)/ γ -zeolite can decrease the beginning temperature of decomposition, however both Fe(II) and Fe(III)/ γ -zeolite catalysts have only slight effect to the T_{max} . The apparent kinetic parameters for ELV thermal and thermo-catalytic pyrolysis between 5 and 95% conversion are summarized in Table 3.

Table 3
Apparent kinetic parameters for ELV thermal and thermo-catalytic pyrolysis (conversion: 5-95%)

	Ea (kJ/mol)	A (min ⁻¹)	R ²
No-catalyst	221	21.832	0.996
ZSM-5	92	1.828	0.981
H/ZSM-5	102	1.438	0.983
Ce/ZSM-5	180	16.083	0.976
Cu/ZSM-5	182	16.285	0.966
Fe(II)/ZSM-5	166	15.995	0.989
Fe(III)/ZSM-5	163	11.507	0.962
Mg/ZSM-5	175	14.778	0.947
Ni/ZSM-5	171	12.986	0.988
Sn/ZSM-5	152	6.605	0.983
Zn/ZSM-5	160	17.681	0.984
γ-zeolite	90	1.676	0.976
H/γ-zeolite	91	1.476	0.955
Ce/γ-zeolite	134	8.322	0.988
Cu/γ-zeolite	140	9.196	0.988
Fe(II)/γ-zeolite	113	5.165	0.992
Fe(III)/γ-zeolite	121	14.18	0.996
Mg/γ-zeolite	131	2.524	0.979

Ni/y-zeolite	129	10.906	0.949
Sn/y-zeolite	111	6.220	0.976
Zn/y-zeolite	116	5.278	0.979

The apparent activation energy of the decomposition is 221kJ/mol without catalyst, which was lower by both modified ZSM-5 and y-zeolite catalysts. It is important to remark, that either parent ZSM-5 or y-zeolite catalysts result in the lowest activation energies among catalysts; 92 and 90kJ/mol, respectively. Both parent catalysts have one of the highest BET surface areas and Si/Al ratios. Y-zeolite catalyst has nearly double BET and BJH surface area, and lower microporous surface area than ZSM-5 catalyst. Because of the similar values of the activation energy and significant difference in surface areas, it can be said, that the decomposition of polymer chain occur in the micropore (1.7-2 nm), mesopore (2–50 nm), and the macropore (50–100 nm). Whereas, the limited microporous surface area for C-C decomposition are compensated by the higher possibility for pyrolysis on larger meso- and macropores in case of y-zeolite. The high value of the Si/Al ratio is also critical. Regarding the metal loaded catalysts, higher values of the activation energies are found. The proton exchange has the less effect to the decomposition reactions, comparing parent catalysts. Only slight difference in activation energies – 102 and 91kJ/mol – was found by the using of H/ZSM-5 and y-zeolite catalysts. Both of them have high surface areas and Si/Al ratios. On the other hand, they were not able to accelerate the C-C scission reactions and accelerate the decomposition of waste ELV raw material, as well. The catalyst efficiency in activation energy decreasing was calculated by the following equation:

$$\eta_{catalyst} = E_a(\text{without catalyst}) - E_a(\text{with catalyst}) \cdot 100$$

where $E_a(\text{without catalyst})$ is the apparent activation energy of the decomposition using only ELV raw material, $E_a(\text{with catalyst})$ is the activation energy of the pyrolysis using different catalysts, too.

Figure 8 shows the catalyst efficiency in apparent activation energy decreasing. As it was before mentioned, both parent and H form catalysts (ZSM-5 and y-zeolite) can decrease the activation energy in the highest degree. On the other hand, the activity of metal loaded catalysts is lower for promoting the decomposition of waste ELV. It is also clear, that y-zeolite based catalysts are more efficient in activation energy decreasing than ZSM-5 based catalysts. Thermo-catalytic pyrolysis of waste ELV by the use of metal loaded y-zeolite catalysts resulted apparent activation energy from 111kJ/kg (Sn/y-zeolite) to 140kJ/mol (Cu/y-zeolite). Whereas metal loaded ZSM-5 modified catalysts showed less effect in activation energy decreasing, because the apparent activation energy changed between 150kJ/mol (Sn/ZSM-5) and 182kJ/mol (Cu/ZSM-5). It is interesting

result, that same order in catalyst efficiency in activation energy decreasing effect was found in case of both modified ZSM-5 and γ -zeolite based catalysts: Cu<Ce<Mg<Ni<Fe(III)<Fe(II)<Zn<Sn.

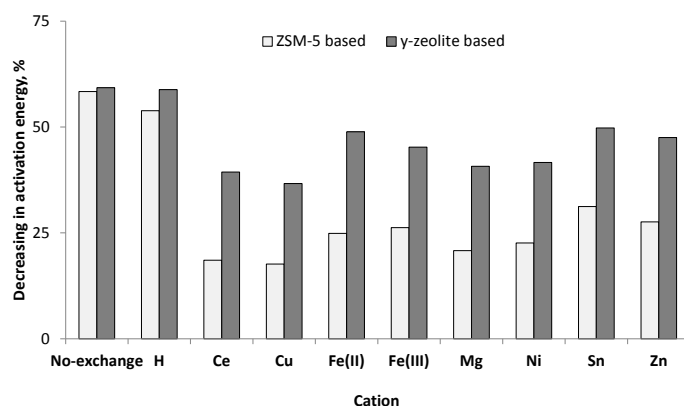


Figure 8
Catalyst efficiency in apparent activation energy decreasing

4. Conclusion

In this work modified ZSM-5 and γ -zeolite catalysts had been synthesized by metal loading and their catalytic effect were investigated using real ELV waste polymers. BET and BJH surface areas, and Si/Al ratios of catalysts can be decreased by metal loading; however the grain size distributions were not changed significantly. The metal content of the treated catalysts were between 8.5% and 9.8%. Catalysts affected the decomposition reactions, because the weight loss curves are shifted to the lower temperature ranges in the presence of catalysts. Regarding the apparent activation energy, it was concluded, that both parent and H form catalysts (ZSM-5 and γ -zeolite) can decrease the activation energy in the highest degree. However, γ -zeolite based catalysts showed higher efficiency than ZSM-5 based. Comparing catalysts, the following order in activation energy decreasing was found: Cu, Ce, Mg, Ni, Fe(III), Fe(II), Zn, Sn, H, non-modified. Results also demonstrate, that BET surface area and Si/Al ratio have great effect to the catalyst efficiency, because large surface areas and high Si/Al ratios favour to pyrolysis reactions. Large BET surface area can decrease the starting of decomposition, while high Si/Al ratios had an important play in T_{max} decreasing. There was no correlation between the BJH surface areas and catalyst activity.”

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References

- [1] P. Harshal, S.M. Lawankar, Waste plastic pyrolysis oil alternative fuel for CI engine – A Review, *Res. J. Engineering Sci.* 2 (2013) 26-34.
- [2] A. Veses, B. Puértolas, M.S. Callén, T. García, Catalytic upgrading of biomass derived pyrolysis vapors over metal-loaded ZSM-5 zeolites: Effect of different metal cations on the bio-oil final properties, *Micropor. Mesopor. Mat.* 209 (2015) 189-196.
- [3] H. Inokawa, S. Nishimoto, Y. Kameshima, M. Miyake, Difference in the catalytic activity of transition metals and their cations loaded in zeolite Y for ethanol steam reforming, *Int. J. Hydrogen Energ.* 35 (2010) 11719-11724.
- [4] R. Miandad, M.A. Barakat, Asad S. Aburizaiza, M. Rehan, A.S. Nizami, Catalytic pyrolysis of plastics waste: A review, *Process Saf. Environ. Prot.* 102 (2016) 822-838.
- [5] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, *Renew. Sustain. Energy Rev.* 73 (2017) 346-368.
- [6] G. Ciobanu, D. Ignat, G. Carja, S. Ratoi, C. Luca, Zinc-modified forms of zeolites by wet impregnation method, *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)* 53 (2008) 200-203.
- [7] J.F. Mastral, C. Berrueco, M. Gea, J. Ceamanos, Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite, *Polym. Degrad. Stab.* 91 (2006) 3330-3338.
- [8] Y.-H. Lin, H.-Y. Yen, Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons, *Polym. Degrad. Stab.* 89 (2005) 101-108.
- [9] M.R. Hernandez, A.N. Garcia, A. Marcilla, Study of the gases obtained in thermal and catalytic flash pyrolysis of HDPE in a fluidized bed reactor, *J. Anal. Appl. Pyrolysis* 73 (2005) 314-322.
- [10] C. Muhammad, J.A. Onwudili, P.T. Williams, Catalytic pyrolysis of waste plastic from electrical and electronic equipment, *J. Anal. Appl. Pyrolysis* 113 (2015) 332-339.
- [11] J. Aguado, D.P. Serrano, G.S. Miguel, M.C. Castro, S. Madrid, Feedstock recycling of polyethylene in a two-step thermos-catalytic reaction system, *J. Anal. Appl. Pyrolysis* 79 (2007) 415-423.
- [12] A. Marcilla, A. Gomez-Siurana, F. Valdes, Catalytic pyrolysis of LDPE over H-beta and HZSM-5 zeolites in dynamic conditions. Study of the evolution of the process, *J. Anal. Appl. Pyrolysis* 79 (2007) 433-442.

- [13] R.K. Balakrishnan, C. Guria, Thermal degradation of polystyrene in the presence of hydrogen by catalyst in solution, *Polym. Degrad. Stab.* 92 (2007) 1583-1591.
- [14] R. Bagri, P.T. Williams, Catalytic pyrolysis of polyethylene, *J. Anal. Appl. Pyrolysis* 63 (2002) 29-41.
- [15] B. Kunwar, B.R. Moser, S.R. Chandrasekaran, N. Rajagopalan, B.K. Sharma, Catalytic and thermal depolymerisation of low value post-consumer high density polyethylene plastic, *Energy* 111 (2016) 884-892.
- [16] G. Elordi, M. Olazar, M. Artetxe, P. Castano, J. Bilbao, Effect of the acidity of the HZSM-5 zeolite catalyst on the cracking of high density polyethylene in a conical spouted bed reactor, *Appl. Catal. A-Gen.* 415-416 (2012) 89-95.
- [17] M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Olazar, Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity, *Ind. Eng. Chem. Res.* 52 (2013) 10637-10645.
- [18] G. Elordi, M. Olazar, G. Lopez, M. Artetxe, J. Bilbao, Continuous polyolefin cracking on an HZSM-5 zeolite catalyst in a conical spouted bed reactor, *Ind. Eng. Chem. Res.* 50 (2011) 6061-6070.
- [19] G. Elordi, M. Olazar, G. Lopez, M. Amutio, M. Artetxe, R. Aguado, J. Bilbao, Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor, *J. Anal. Appl. Pyrolysis* 85 (2009) 345-351.
- [20] C. Vasile, H. Pakdel, B. Mihai, P. Onu, H. Darie, S. Ciocalteu, Thermal and catalytic decomposition of mixed plastics, *J. Anal. Appl. Pyrolysis* 57 (2001) 287-303.
- [21] A. Marcilla, M.I. Beltran, R. Navarro, Thermal and catalytic pyrolysis of polyethylene over HZSM-5 and HUSY zeolites in a batch reactor under dynamic conditions, *App. Catal. B-Environ.* 86 (2009) 78-86.
- [22] Ch. Baerlocher, D.H. Olson, W.M. Meier, *Atlas of zeolite framework types*, fifth ed., Elsevier, Amsterdam, 2001.
- [23] Y. Wang, J. Wang, Multifaceted effects of HZSM-5 (Proton-exchanged Zeolite Socony Mobil-5) on catalytic cracking of pinewood pyrolysis vapor in a two-stage fixed bed reactor, *Biores. Technol.* 214 (2016) 700-710.
- [24] W.J. Hall, N. Zakaria, P.T. Williams, Pyrolysis of latex gloves in the presence of Y-zeolite, *Waste Manage.* 29 (2009) 797-803.
- [25] O.D. Mante, F.A. Agblevor, S.T. Oyama, R. McClund, Catalytic pyrolysis with ZSM-5 based additive as co-catalyst to Y-zeolite in two reactor configurations, *Fuel* 117 (2014) 649-659.

- [26] Y. Zhang, Y. Zhou, L. Huang, S. Zhou, X. Sheng, Q. Wang, C. Zhang, Structure and catalytic properties of the Zn-modified ZSM-5 supported platinum catalyst for propane dehydrogenation, *Chem. Eng. J.* 270 (2015) 352-361.
- [27] S. Vichaphund, D. Ahtong, V. Sricharoenchaikul, D. Atong, Production of aromatic compounds from catalytic fast pyrolysis of *Jatropha* residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods, *Renew. Energ.* 79 (2015) 28-37.
- [28] T.L. Liu, J.P. Cao, X.Y. Zhao, J.X. W., X.Y. Ren, X. Fan, Y.P. Zhao, X.Y. Wei, In situ upgrading of Shengli lignite pyrolysis vapors over metal-loaded HZSM-5 catalyst, *Fuel Process. Technol.* 160 (2017) 19-26.
- [29] E.F. Iliopoulou, D. Stefanidis, K.G. Kalogiannis, A. Delimitis, A.A. Lappas, K.S. Triantafyllidis, Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite, *App. Catal. B-Environ.* 127 (2012) 281-290.
- [30] L. Wang, H. Lei, Q. Bu, S. Ren, Y. Wei, L. Zhu, X. Zhang, Y. Liu, G. Yadavalli, J. Lee, S. Chen, J. Tang, Aromatic hydrocarbons production from ex situ catalysis of pyrolysis vapor over Zinc modified ZSM-5 in a packed-bed catalysis coupled with microwave pyrolysis reactor, *Fuel* 129 (2014) 78-85.
- [31] J. Feroso, H. Hernando, P. Jana, I. Moreno, J. Přech, C. Ochoa-Hernández, P. Pizarro, J.M. Coronado, J. Čejka, D.P. Serrano, Lamellar and pillared ZSM-5 zeolites modified with MgO and ZnO for catalytic fast-pyrolysis of eucalyptus woodchips, *Catal. Today.* 277 (2016) 171-181.