

# Production of Hydrogen Rich Products from Mixture of Polyolefin and PET over Different Modified ZSM-5 Catalysts

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The goal of this work was the production of hydrogen rich fraction and high value added products by pyrolysis of waste plastics over zeolite catalysts. The effects of Si/Al ratios: 22.5, 49.1 and 65.5 on product yields were also investigated. Raw materials (polyolefin) and polyethylene terephthalate (PET)) were placed in a horizontal tubular furnace. For pyrolysis, high temperature and nitrogen flow was used. It was found, that the transition metal incorporated into the structure of synthetic zeolite had an advanced effect to the hydrogen yield and isomerization. Acidic catalysts with high Si/Al ratio can also support the decomposition of C-C bonds, maximize the yields of gaseous products and minimize the amount of pyrolysis oil. The maximum hydrogen production (47.0 %) was achieved over Ni/ZSM-5 catalyst. This was happened due to the presence of nickel in the catalyst which increasing the conversion rate. Pyrolysis oil contains high content of aromatic compounds, which was caused by the structure of PET waste and isomerization effect of ZSM-5 catalyst. For hydrogen both the aromatization reactions and the high concentration of unsaturated branched compounds could be blamed.

Keywords: pyrolysis, PET, polyolefin, hydrogen, metal loaded catalysts, transition metal

## 1. Introduction

The world energy consumption is rapidly increasing, which leads to energy tautness and harms the environment, i.e. release of pollutant and the decrease of fossil fuel reserves. Vast amount of energy is needed for transportation, industry and residential. Nowadays mainly the fossil energy sources are used; coal, crude oil and natural gas. However, hydrogen is considered as one of the promising energy sources (Wanga and Cheng, 2012), and will become a significant carrier energy in the future. Hydrogen is a promising energy that potentially plays an important role in future energy systems due to its clean burning qualities. On the other hand, the increasing consumption of plastics for different purposes caused serious environmental problems, because the waste plastics are non-biodegradable and chemically resistance so it can harms the living organisms. Polyethylene, polypropylene, polyethylene terephthalate, polystyrene and poly vinyl chloride are represented in the highest amount in waste plastic streams (Bungay, 2017). Most of the processes for waste treatment (e.g. landfilling, incineration) are not useful due to the released of toxic gases and chemicals to the environment. Therefore, finding an alternative way for recycling these wastes can save the environment from its pollution. Due to immiscible phase separation, mechanical recycling of waste plastics is also difficult to apply for mixed or contaminated plastic waste utilization.

Pyrolysis is considered as one of the most suitable technique for converting waste plastics into high value products such as hydrogen. Furthermore, it is one of the most environmentally technique for waste plastics recycling (Barbarias et al., 2015). In pyrolysis reaction, high temperature (higher than 600 °C) is favoured for high conversion of waste plastics. Nowadays, most of researches are focusing on the use of new catalysts to improve and increased the production selectivity (Panda et al., 2010). Nickel, cobalt, iron are relatively inexpensive and promising catalysts for biomass and waste plastic pyrolysis or gasification (Bulushev and Ross, 2011). Regarding the catalysts, ZSM-5 have been used widely in pyrolysis due to it is ability to promote the decomposition reaction of waste plastics. Gao et al., (2010) tested different catalysts in the pyrolysis of

waste plastics and founded that ZSM-5 was the best catalyst between all the tested zeolite catalysts. Additionally, the good performance of ZSM-5 in pyrolysis process can be attributed to its shape selective pore structure (Du et al., 2016). It is also well known, that the catalytic effect is attributed to the Si/Al ratio of the catalysts, the catalyst pore channel, surface area, acidity, etc. In general, higher surface area, higher Si/Al ratio and acidity of the catalysts led to higher yields of gases and pyrolysis oil due to the more intensive broken of the C-C bonds. The goal of this work was the investigation of the pyrolysis of 50%/50% polyolefin and polyethylene terephthalate waste plastics at 700 °C temperature in tubular furnace using different active metals supported by ZSM-5 catalyst, focusing on the effect of catalysts type and Si/Al ratio on the pyrolysis process. Especially the product yields and the compositions of gaseous and pyrolysis oil fraction were discussed.

## 2. Raw materials and methods

### 2.1 Raw materials

Municipal waste plastics, such as low density polyethylene (29 %), high density polyethylene (21 %) and polyethylene terephthalate (50 %) were used as raw materials from municipal sources. Raw materials were shredded and milled by laboratory grinder (Dipre GRS 183A9) into small particles.

Synthetic aluminosilicate (ZSM-5 type,  $\text{NaAlSi}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ ) zeolite catalysts with different silica-alumina ratios (Si/Al= 22.5, 41.9 and 65.5) were used to modify the product yields and composition. Catalyst had pentasil units, connected via oxygen bridges, with ~5 Å channel size. Both synthetic aluminosilicate catalysts were modified by wet impregnation. Aluminosilicates were added into 1M  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , V-EDTA,  $\text{ZnCl}_2$  dissolution and continuously stirred for 2 h at 85 °C. Then catalysts were dried for 10 h at 110 °C, and conditioned at 650 °C for 5 h in air.

### 2.2 Raw materials

Raw materials were pyrolyzed in a tubular furnace at 700 °C using 2.5 dm<sup>3</sup>/h nitrogen flow (Figure 1). 5 g of raw materials and 2.5 g of the catalysts were placed in the quartz tube separated from each other by quartz wool. The reaction time was 20 minutes at the set temperature, then the reactor was disassembled, when the temperature reach the 300 °C. Volatiles from reactor were cooled by cryostat using 10 °C, where the pyrolysis oil was condensed. Gaseous product was collected into a Tedlar bag. At the end of the reactions, products were weighted and their yields were calculated based on the weight balance.

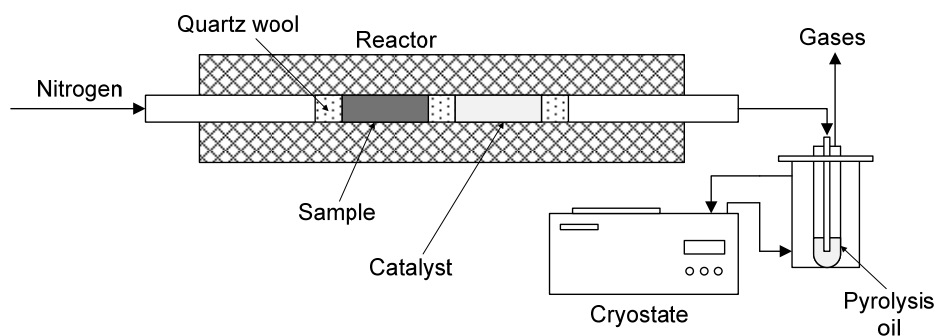


Figure 1: Horizontal tubular furnace for waste pyrolysis

### 2.3 Product analysis

Hydrocarbons in gases were investigated by a GC-FID (DANI GC) using Rtx PONA (100 m x 0.25 mm, surface thickness of 0.5 µm) and Rtx-5 PONA (100 m x 0.25 mm, surface thickness of 1 µm) columns. Sample analysis was taken using isotherm conditions (T=30 °C).

The hydrogen content in gases was measured by GC-TCD (Shimadzu GC-2010) using Carboxen<sup>TM</sup> 1006 PLOT column (30 m x 0.53 mm). The initial temperature was 35 °C (hold time 2 min), then it was elevated to 250 °C at 40 °C min<sup>-1</sup> heating rate and the final temperature maintained for 5 min.

Pyrolysis oil was analysed by GC-FID (DANI GC), using Rtx 1 dimetil-polysiloxan capillary column (30 m x 0.53 mm, thickness of 0.25 µm). Sample was dissolved in CS<sub>2</sub>, and then injected to the instrument. The initial temperature was 40 °C for 5 min, then the temperature was elevated by 8 °C/min till 340 °C and it was kept at 340 °C till 20 min. Both the injector and detector temperature were 340 °C.

### 3. Result and discussion

#### 3.1 Product yields

The decomposition products (gases, pyrolysis oil and char) from the pyrolysis experiments using catalysts with different Si/Al ratio are summarized in Figure 2 (a, b, c). The results well indicated that the yields of gases for the different ZSM-5 type catalysts with Si/Al ratios are much higher in comparison to the other two products. That phenomenon was the consequence of the high temperature (700 °C) in tubular furnace. It can be also seen that gaseous products over nickel supported by ZSM-5 catalyst for any Si/Al ratios was higher compared to the others four catalysts. This behavior corresponds to the presence of Ni in the catalyst that caused reaction accelerated and increasing in smaller compounds, such as gaseous products (Kumagai et al., 2015). Furthermore, this is in agreement with experimental results of e.g. Iliopoulou et al. (2012), who found that Ni modified catalyst resulted higher gas yield in pyrolysis reaction. On the other hand, Zn supported by ZSM-5 catalyst had the less effect to the pyrolysis experiments because that catalyst had the lower gases product, which is 55.7 %, 67.7 % and 86.6% for the ZSM-5 with Si/Al ratio of 22.5, 41.9 and 65.5, respectively.

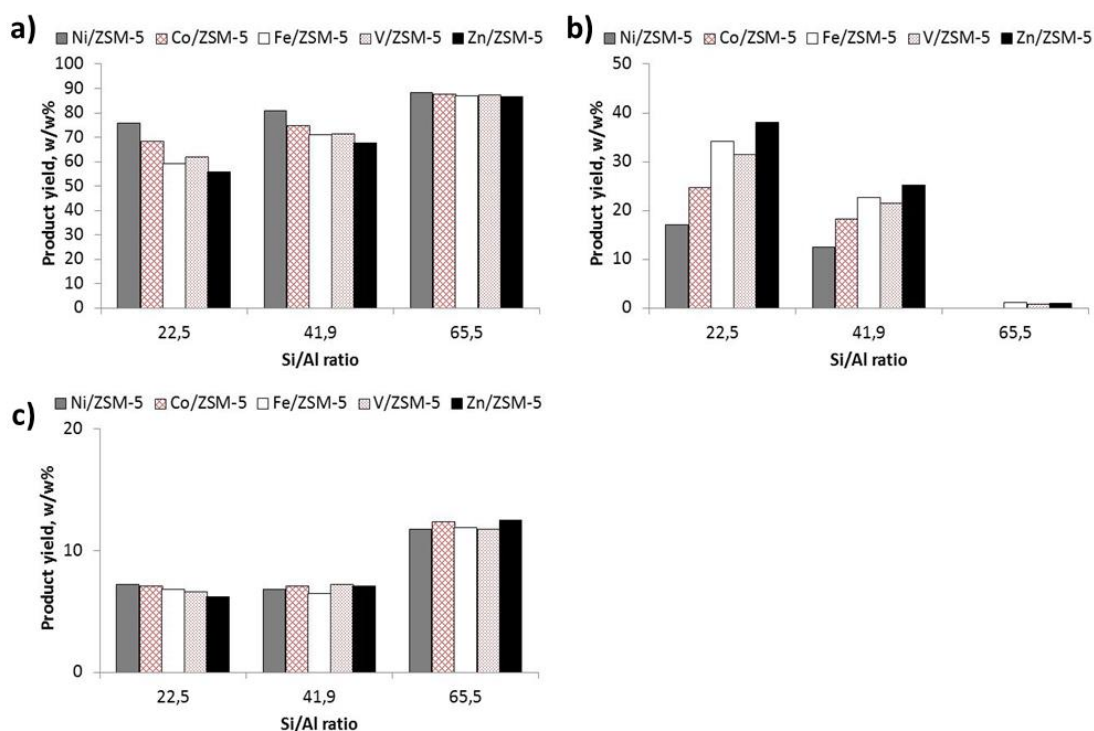


Figure 2: Product yields using ZSM-5 catalysts (gases (a), pyrolysis oil (b) and char (c))

Regarding high Si/Al ratio, it is clear, that basically gasification was taken place, because the yield of pyrolysis oil was less than 1.1 %. Catalysts with higher Si/Al ratio had considerable lower yields of pyrolysis oil, higher yields of gases; however, the yields of char did not change by the Si/Al ratio from 22.5 to 41.9. On the other hand, it is also well shown, that significant increasing in solid char was found, when the Si/Al ratio increased from 41.9 to 65.5. E.g. the yield of pyrolysis oil was between 17.1 % (Ni/ZSM-5) and 38.1 % (Zn/ZSM-5) using ZSM-5 catalysts with Si/Al ratio of 22.1, while that of was between 12.4 % (Ni/ZSM-5) and 25.2 % (Zn/ZSM-5). For this result the C-C bond breaking effect of the catalyst with higher Si/Al ratio could be blamed. As is well known, the C-C bonds of polymer molecules are broken by the ions formed in the initiation reaction step. The higher Si/Al ratio of the catalysts is favors for the formation of these ions. Although, owing to the rapid blockage of the catalyst pore mouth, the too high Si/Al ratio of the catalyst is quite often led to very quick deactivation of the catalyst. It is strange result, that the type of transition metal on catalyst support had no effect to the char yields. Notable difference among the yields of char obtained by the using of different catalysts cannot be found. Regarding the high char deposition obtained on 65.5 Si/Al ratio, especially the Boudouard reaction ( $2\text{CO}=\text{CO}_2+\text{C}$ ) can be blamed.

### 3.2 Gases

The compositions of gases are summarized in Figure 3 (a-f), which shows the effect of catalyst type and Si/Al ratio on the decomposition reaction. Gases contain H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, branched and non-branched hydrocarbons (up to C<sub>5</sub>).

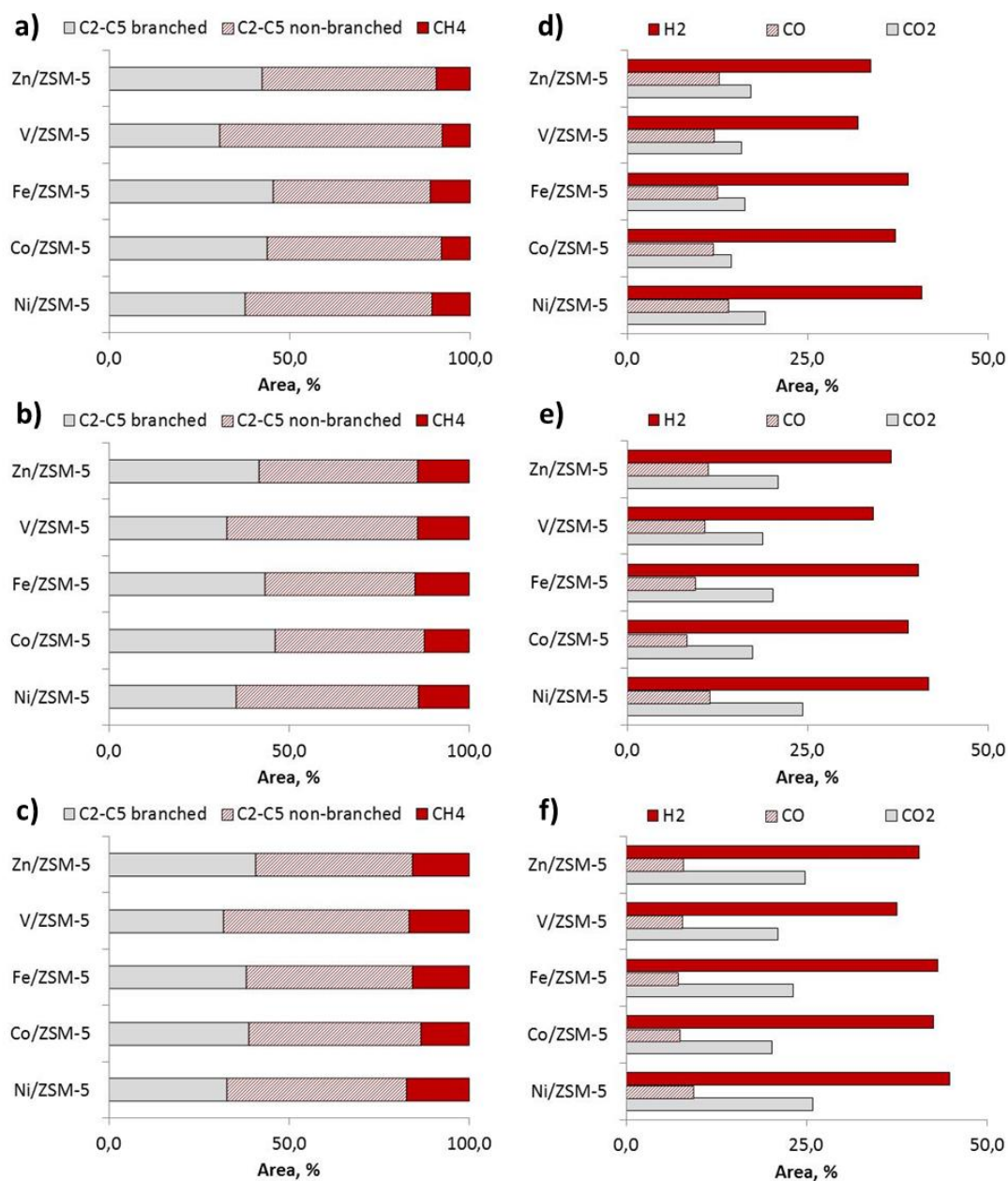


Figure 3: Gas composition by GC-FID and GC-TCD using ZSM-5 catalysts (Si/Al=22.5 (a, d), Si/Al=41.9 (b, e) and Si/Al=65.5 (c, f))

Regarding the GC-FID results, the concentration of methane was changed slightly with changing the catalyst type and Si/Al ratio. The normalized concentration of methane was 7.5 % (Fe/ZSM-5)-10.7 % (V/ZSM-5) using catalysts with Si/Al ratio of 22.5, while it was 13.3 % (Co/ZSM-5)-17.1 % (Ni/ZSM-5) using catalysts with 65.5 Si/Al ratio. The higher methane content of the gases obtained by catalysts with higher Si/Al ratio could be explained with the higher activity in C-C scission of those catalysts. Regarding the non-branched hydrocarbons, the dominant presence of ethane and ethane was observed. On the other hand, the concentrations of unsaturated hydrocarbons were always higher, than the saturated using any catalysts. It is

important to remark, that the concentration of ethene was significantly higher, while the ethane concentration was lower using catalysts with higher Si/Al ratio, which can be attributed to the higher  $\beta$ -scission activity of the catalysts. However, the high yield of non-branched hydrocarbons was achieved over V/ZSM-5 catalyst with Si/Al ratio of 22.5, while the lowest yield observed over Co/ZSM-5 catalyst with Si/Al ratio of 65.5. Regarding the branched hydrocarbons, especially  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  showed advanced property in isomerization effect, and the  $\text{C}_6$  isomers showed high concentrations; e.g. 2,2 dimethyl butane, 2,3 dimethyl butane, 2-methyl pentene. It is important to remark, that the diolefins (e.g. butadiene) had also concentrations around 3-5 %. The results of GC-TCD show that the hydrogen production over Ni/ZSM-5 catalyst for any Si/Al ratios was the highest compared to the other catalysts that used in the experiments which are 42.7 %, 43.7 % and 47.0 %. This can be attributed to the high conversion rate as a result of Ni presence in the catalyst. The hydrogen gas over V/ZSM-5 catalyst was the lower 33.4 %, 35.8 % and 39.3 % for Si/Al of 22.5, 41.9 and 65.5, respectively. However, the Si/Al ratio of the catalysts affects only slightly the hydrogen content of gases. The decomposition reaction for the polyethylene terephthalate in the raw materials was the caused for CO and  $\text{CO}_2$  in gases product. In general CO had lower concentration than  $\text{CO}_2$ . This is due to the water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ). Higher Si/Al ratio of the catalyst resulted lower concentration of CO and higher concentration of  $\text{CO}_2$ .

### 3.3 Pyrolysis oil

Figure 4 illustrates the compositions of pyrolysis oil by GC-FID. Results indicate that the oil product contained n-olefins, n-paraffin, non-oxygenated aromatics, branched and oxygenated compounds. The concentration of n-paraffin and n-olefin changed with changing both the transition metal on ZSM-5 catalyst support or Si/Al ratio. E.g. the concentration of n-paraffin was 17.0 % and 10.0 % using Ni/ZSM-5 catalysts with Si/Al ratio of 22.5 and 49.1, respectively. In general, due to the higher yields of aromatic and other hydrocarbons, catalysts with higher Si/Al ratio resulted lower concentration of n-paraffin and n-olefin compounds. The ratio of n-saturated and unsaturated compounds was between 0.68-0.88 using catalysts with Si/Al ratio of 22.5 and 0.68-0.87 using catalysts with Si/Al ratio of 49.1. It means that the Si/Al ratio had no effect to the ratio of n-saturated and unsaturated compounds. The Si/Al ratio of the catalysts had more significant effect to the concentration of aromatics, and branched hydrocarbons. The aromatic compounds had the highest yield among the other compounds in the oil product for both Si/Al ratios. The increasing in aromatic compounds was attributed to the high efficiency of ZSM-5 catalyst for cracking the heavy compounds and converted then into aromatics (Miskolczi et al., 2017). Moreover, it is increased slightly with increasing Si/Al=49.1. Especially Ni/ZSM-5 (Si/Al ratio of 49.1) and Co/ZSM-5 (Si/Al ratio of 22.5) catalysts showed efficiency in aromatization reaction. This was happened due to the ability of Si/Al to promote the cracking efficiency (Khaing Thandar Kyaw, 2015). Regarding the branched hydrocarbons it is important to note, that Fe/ZSM-5 catalyst could increase the most significantly the yields of other compounds (branched, etc.).

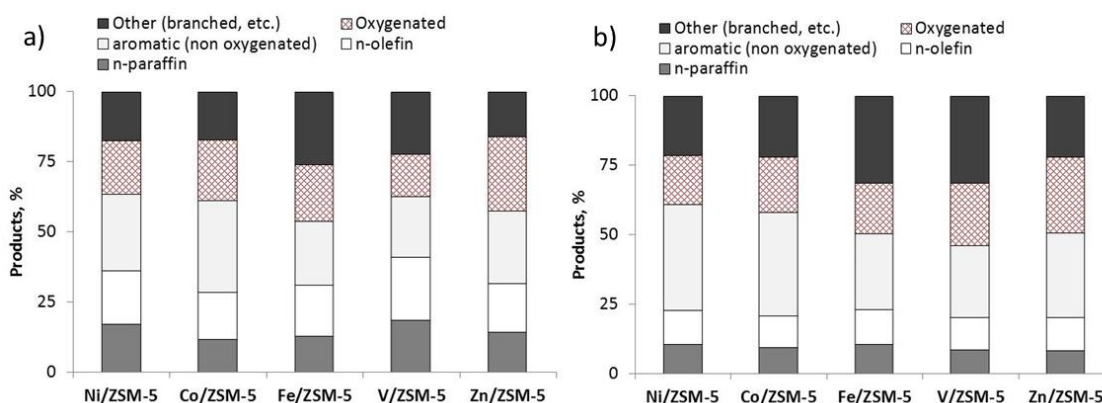


Figure 4: Pyrolysis oil composition using ZSM-5 catalysts by GC-FID (Si/Al=22.5 (a) and Si/Al=41.9 (b))

## 4. Conclusions

In this study, different active metals, supported by ZSM-5 with different Si/Al ratios have been investigated on pyrolysis of real waste HDPE and PET. Pyrolysis experiments of high density polyethylene and polyethylene terephthalate were carried out at temperature of 700 °C. Hydrogen, carbon monoxide, carbon dioxide, methane, branched and non-branched hydrocarbons up to  $\text{C}_5$  were the mainly products in the gas yields. It

was concluded, that both Ni/ZSM-5 and Co/ZSM-5 catalysts resulted in high gas yield. Ni/ZSM-5 catalyst showed higher efficiency than other catalysts. While, the maximum pyrolysis oil yield was achieved over Zn/ZSM-5 catalyst. Results also demonstrate that Si/Al ratio of the catalysts can affect mainly the scission of C-C bonds. Chemical reactions belong to the transition metal sites, such as hydrogen formation, were only slightly changed by Si/Al ratios. However, higher Si/Al ratio can tendentially increase the hydrogen and CO<sub>2</sub> concentration. On the other hand, owing the Boudouard reaction, the char yield was significantly higher using catalysts with 65.5 Si/Al ratios.

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