High Temperature Pyrolysis of Municipal Plastic Waste Using Me/Ni/ZSM-5 Catalysts: The Effect of Metal/Nickel Ratio

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Abstract: This work is dedicated to the high temperature pyrolysis of municipal plastic waste using Me/Ni/ZSM-5 catalysts. Catalysts were synthetized by wet impregnation. In addition to nickel, synthetic zeolite catalysts contain calcium, ceria, lanthanum, magnesia or manganese. Catalysts were prepared and tested using 0.1, 0.5 and 2.0 Me/Ni ratios. Catalyst morphology was investigated by SEM and surface analysis. Higher concentrations of second metals can block catalyst pore channels due to the more coke formation, which leads to smaller surface area. Furthermore, the chemicals used for the impregnation were among the catalyst grains, especially in case of 2.0 Me/Ni ratios. For pyrolysis, a horizontal tubular furnace reactor was used at 700 °C. The highest hydrogen and syngas yields were observed using ceria- and lanthanum-covered catalysts. The maximum production of syngas and hydrogen (69.8 and 49.2 mmol/g raw material) was found in the presence of Ce/Ni/ZSM-5 catalyst with a 0.5 Me/Ni ratio.

Keywords: pyrolysis; waste plastic; syngas; metal loaded catalysts; gas-chromatography

1. Introduction

At present, vast amounts of plastics waste are produced annually due to high demand of plastics for various applications. Polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) represent the main fractions of plastics produced worldwide [1]. The increasing quantities of plastic waste cause serious environmental problems [2]. On one hand, most plastic wastes are treated by landfilling or incineration, which contributes to increased pollution by releasing toxic gases into the atmosphere [3]. One the other hand, energy consumption, especially for transportation, residential and industry, has increased [4]. These mainly rely on non-renewable sources for energy such as fossil fuels, natural gas, oil and coal. Currently, hydrogen promises high potential for energy applications and may play an important role in future energy systems because it could replace fossil energy sources due to its clean burning qualities [5]. Hence, hydrogen production is a matter of great importance, both in clean fuel production and chemical synthesis. Plastics also play a key role among different wastes due to their high energy content. Therefore, waste-to-energy technology is an attractive way for plastic waste recycling to recover their hidden energy content.

Pyrolysis is a widely-investigated possibility for chemical recycling of waste polymers by converting raw materials into valuable products such as hydrogen or other syngas. The pyrolysis process can provide a novel route for the recycling of waste polymers by producing a suite of valuable hydrocarbons. Alkanes such as methane, ethane, propane and butane are the main components of the hydrocarbon gases extracted from pyrolysis of waste polymers, with high proportion of 80%, while...
alkenes represent 10%–20% [6]. However, waste plastics can be converted into valuable hydrocarbons by pyrolysis at high temperature. Therefore, waste-plastic-to-hydrogen followed by synthesis gas production by pyrolysis and gasification processes is another route of waste management. Atmosphere, temperature, feed stock, reactor and catalyst type are the most significant factors that affected the thermal decomposition rate and the production of syngas in the pyrolysis and gasification process. Various types of waste plastics from different sources have been used as feed stocks for this process in order to enhance the syngas and product yields. For example, Saad and Williams [7] performed pyrolysis of different waste plastics which mainly consisted of HDPE (high density poly ethylene), LDPE (low density poly ethylene), PET, PP, PS and PE to produce syngas using two-stage fixed bed reactor. They concluded that using HDPE/PET as raw materials showed the highest syngas yields of 156.45 mmol/g, as compared to other plastic samples. Further, Miandad et al. [8] investigated the influence of different waste plastic feed stocks on oil production using a small pilot-scale reactor. Their results showed that a mixture of PP and PE resulted in better oil yields, as compared to individual plastic feed stocks. Moreover, many studies have reported that syngas yield can be improved by the addition of steam or through partial oxidation [9,10].

Previously, Wu and Williams [11] indicated that gas yield and hydrogen production were improved by introducing steam to the catalytic pyrolysis of waste plastics mixture (HDPE, PP and PS). Regarding the effect of reaction temperature, higher pyrolysis temperatures can greatly influence product composition by increasing the gas product and decreasing the oil product [12,13]. Temperature has a crucial effect on waste plastic decomposition, as the yields of hydrogen and carbon nanotubes are affected by catalyst temperature [14]. A study by [15] reported that the maximum hydrogen yield was observed at the highest reaction temperature, 815 °C.

In catalyst research, various bimetallic catalysts such as Ni, Co, Fe and Cu have been studied in the context of decomposition of waste plastic [16,17]. According to references, the production of hydrogen/syngas can be increased using transition metal-loaded zeolite catalysts (ZSM-5, y-zeolite, y-zeolite, etc.), especially ones that are nickel-based. Nickel-based catalysts have been shown to have a higher efficiency in the pyrolysis process, as higher amounts of hydrogen are produced [18]. Further, nickel-based catalysts show higher efficiency in catalytic pyrolysis due to their high capacity to break C-C chemical bonds [19]. The advantageous properties of nickel-based catalysts are affected by many parameters, especially by the zeolite structure and properties, or even by other metals. In addition, raising the temperature of thermal decomposition reactions is favorable, as a higher gas proportion will be produced in the pyrolysis product [12]. Previously, Liu et al. [20] studied the effects of Ni-based catalysts on the co-gasification of mixtures of biomass and plastic. They found that nickel promoted the production of hydrogen. In another work, Yao et al. investigated the influence of different zeolite-supported nickel catalysts on hydrogen and syngas production from the pyrolysis of waste polyethylene. Ni/ZSM-5, Ni/y-zeolite and Ni/y-zeolite were used and examined for this process. They reported that the Ni/ZSM-5 catalyst had the highest activity compared to other two catalysts, as higher hydrogen and syngas yields were produced [21]. Regarding the catalyst’s promoters, studies have shown that adding some promoters such as Ce, Mg, La and Ca can improve catalyst activity and stability by enhancing physical and chemical properties [22,23]. Moreover, the structure and uniformity of Ni-based catalyst particles can be improved by adding metal promoters, resulting in better metal dispersion [7]. Santamaria et al. [24] studied the effect of La2O3 addition on a nickel-based catalyst in the pyrolysis of biomass. They reported that the catalyst Ni/La2O3-Al2O3 showed higher stability and better performance than Ni/Al2O3 in terms of hydrogen production. In another work, Nahil et al. [25] investigated the influence of the addition of metal to Ni-based catalysts for hydrogen production from pyrolysis of waste polypropylene. They indicated that hydrogen yield was increased with the addition of Mn to the catalyst.

In this work, bimetallic catalysts with different Me/Ni ratios were prepared and used for pyrolysis of real waste materials at 700 °C in a horizontal tubular reactor. Five different promoters (Ce, La, Mg,
Ca and Mn) were used to support the Ni/ZSM-5 catalyst in order to enhance the catalysts’ performance towards product yields.

2. Materials and Methods

2.1. Raw Material

Municipal plastic waste as a mixture of low-density polyethylene (17%), high-density polyethylene (14%), polypropylene (19%), polyethylene terephthalate (45%) and others (5%) was obtained from selective waste collection islands from Hungary (yellow (plastic) bin). Each piece of plastic waste was investigated by FTIR, and the type of plastic was determined based on its infrared spectra. The percent composition by weight of the raw material was determined based on the weight of the basic pieces. Larger non-plastic items (e.g., Tetra Paks) were separated from the plastics before the plastics were shredded and milled into small particles before pyrolysis. Raw materials were 72% carbon, 11% hydrogen, 16% oxygen and 1% nitrogen. The ash content was 2.4%.

2.2. Catalysts

The product yields and composition were modified by metal-impregnated ZSM-5 catalyst. The main properties of the catalysts are summarized in Table 1.

| MeNi/ZSM-5 | S_BJH, m²/g | S_micro, m²/g | BET, m²/g | Average Grain Diameter, µm |
|------------|-------------|-------------|----------|--------------------------|
| 0.1 CeNi/ZSM-5 | 94.2        | 325         | 464      | 0.74                     |
| 0.1 LaNi/ZSM-5 | 95.1        | 320         | 461      | 0.56                     |
| 0.1 MgNi/ZSM-5 | 92.6        | 315         | 465      | 0.69                     |
| 0.1 CaNi/ZSM-5 | 92.4        | 318         | 460      | 0.62                     |
| 0.1 MnNi/ZSM-5 | 91.9        | 322         | 466      | 0.64                     |
| 0.5 CeNi/ZSM-5 | 92.7        | 311         | 445      | 0.83                     |
| 0.5 LaNi/ZSM-5 | 90.9        | 305         | 408      | 0.63                     |
| 0.5 MgNi/ZSM-5 | 89.5        | 288         | 404      | 0.57                     |
| 0.5 CaNi/ZSM-5 | 93.8        | 210         | 419      | 0.73                     |
| 0.5 MnNi/ZSM-5 | 92.4        | 281         | 395      | 0.87                     |
| 2.0 CeNi/ZSM-5 | 91.1        | 280         | 359      | 1.16                     |
| 2.0 LaNi/ZSM-5 | 93.5        | 285         | 362      | 0.96                     |
| 2.0 MgNi/ZSM-5 | 92.6        | 257         | 355      | 1.04                     |
| 2.0 CaNi/ZSM-5 | 91.4        | 195         | 350      | 1.28                     |
| 2.0 MnNi/ZSM-5 | 95.2        | 258         | 361      | 0.76                     |

The average grain diameter of the catalysts was investigated using a Fritsch Analysette 22 instrument according to Fraunhofer theory. The morphology of the catalysts was analyzed by N2 adsorption/desorption isotherms using Micromeritics ASAP 2000-type instrument (ASAP 2000 operational program V1.03). A 1 g sample of catalyst was outgassed under vacuum at 160 °C. The BET (Brunauer-Emmett-Teller) method was used for the determination of surface areas based on nitrogen adsorption isotherms, while the S_BJH was calculated using the nitrogen desorption isotherms based on the BJH (Barrett-Joyner-Halenda) model. SEM methods (FEI Thermo Fisher Apreo S LoVac instrument, EDAX AMETEK Octane Elect Plus) were used to examine the morphology and elemental composition of the catalysts. The pentasil units (eight five-membered rings) are linked through oxygen atoms in the ZSM-5 structure, containing 10 ring-holes measuring 5.4–5.6 Å. The tested MeNi/ZSM-5 (Me = Ce, La, Mg, Ca, Mn) catalysts were prepared by wet impregnation. The two metals were used in different MeNi ratios: 0.1, 0.5 and 2.0. First, Ni/ZSM-5 was synthesized. The ZSM-5 synthetic zeolite was impregnated by dissolution of Ni(NO₃)₂·6H₂O, then the produced Ni/ZSM-5 catalyst was dried (10 h, 110 °C) and treated at 650 °C for 5 h in air. To add the second metal promoters, CaCl₂ (Reanal...
Kft, Hungary), CeSO$_4$·4H$_2$O (Reanal Kft, Hungary), LaCl$_3$·7H$_2$O (Reanal Kft, Hungary), Mg(NO$_3$)$_2$ (Sigma-Aldrich) and MnCl$_2$·4H$_2$O (Reanal Kft, Hungary) were dissolved in deionized water in different concentrations, then stirred for 2 h at 85 °C. After that, the Me/Ni/ZSM-5 catalysts were dried for 10 h at 110 °C then conditioned with air for 5 h at 600 °C. The Ni content of the catalysts was between 3.83% and 4.12%. The secondary metals (Me = Ce, La, Mg, Ca and Mn) were used in three different concentration ranges: 0.41%–0.48%, 1.97%–2.11% and 7.70%–8.51% (Table 2).

| Table 2. Elemental composition of the catalysts. |
|-----------------------------------------------|
| **Catalyst Surface Area**                      |
| **Catalyst Grain Surface**                     |
| Me, %  | Ni, %  | O, %  | Si/Al | Me, %  | Ni, %  | O, %  | Si/Al |
|--------|--------|-------|-------|--------|--------|-------|-------|
| 0.1 Ce/Ni/ZSM-5  | 0.41  | 3.83 | 60.98  | 30.09 | 0.39  | 3.85 | 61.04  | 30.81 |
| 0.1 La/Ni/ZSM-5  | 0.42  | 3.86 | 58.57  | 30.89 | 0.42  | 3.87 | 59.74  | 31.63 |
| 0.1 Mg/Ni/ZSM-5  | 0.48  | 3.88 | 58.63  | 32.44 | 0.46  | 3.88 | 60.70  | 30.55 |
| 0.1 Ca/Ni/ZSM-5  | 0.44  | 4.10 | 57.31  | 29.52 | 0.44  | 4.27 | 59.92  | 30.79 |
| 0.5 Ce/Ni/ZSM-5  | 2.11  | 3.89 | 60.53  | 30.53 | 2.03  | 4.02 | 59.35  | 30.94 |
| 0.5 La/Ni/ZSM-5  | 2.04  | 3.83 | 58.19  | 31.83 | 1.93  | 3.76 | 59.16  | 31.82 |
| 0.5 Mg/Ni/ZSM-5  | 1.97  | 3.85 | 57.10  | 30.62 | 1.92  | 3.84 | 57.51  | 30.78 |
| 0.5 Ca/Ni/ZSM-5  | 2.05  | 3.90 | 60.27  | 30.24 | 1.92  | 3.73 | 58.97  | 32.15 |
| 0.5 Mn/Ni/ZSM-5  | 2.05  | 3.88 | 57.41  | 31.74 | 1.99  | 3.79 | 57.10  | 30.24 |
| 2.0 Ce/Ni/ZSM-5  | 7.70  | 3.87 | 58.35  | 31.07 | 7.37  | 3.67 | 58.06  | 31.91 |
| 2.0 La/Ni/ZSM-5  | 7.72  | 3.83 | 56.55  | 32.35 | 7.14  | 3.52 | 57.83  | 31.87 |
| 2.0 Mg/Ni/ZSM-5  | 8.38  | 3.84 | 56.79  | 31.17 | 7.55  | 3.82 | 58.84  | 30.93 |
| 2.0 Ca/Ni/ZSM-5  | 8.51  | 3.93 | 59.63  | 31.48 | 8.02  | 4.05 | 60.40  | 30.46 |
| 2.0 Mn/Ni/ZSM-5  | 8.03  | 3.86 | 57.42  | 30.36 | 7.55  | 3.77 | 58.21  | 30.53 |

The results show that the Si/Al ratio did not change with impregnation; however, the morphological characteristics changed noticeably. The average grain diameter of the catalysts increased slightly at higher Me concentrations (from 0.62–0.74 to 0.76–1.28 µm). In parallel, the BET, BHJ and microporous surface areas were significantly reduced. For example, the BET surface area was reduced from 460–464 to 350–362 m$^2$/g when the Me/Ni ratio was increased from 0.1 to 2.0. The oxygen content of the catalysts was between 56.55% and 60.98% and was not affected by the Me/Ni ratio.

The morphology of the catalysts was investigated using the SEM method. Figure 1 shows the SEM micrographs of the impregnated catalysts.

The micrographs clearly show that larger catalyst agglomerates were formed at higher Me/Ni ratios. Furthermore, the compounds used as impregnating agents can be found among the catalyst particles at higher concentrations of the impregnating agent. This phenomenon is clearly shown especially at a 2.0 Me/Ni ratio. On the other hand, the elemental composition of the catalyst grain corresponds to slight differences between the composition of the catalyst grain and the surface area of the majority of the catalyst particles.

Table 2 summarises the elemental composition of one catalyst grain and the given surface area of the catalyst (containing grains and impregnation compounds among the catalyst grains). Studies indicate that catalyst particles are not capable of absorbing more ions than a certain concentration of the impregnating cation at a given concentration. This is also partly the reason for the aforementioned reduction in the pore surface areas, as the ions of the solution used as the impregnating agent can cover the channels of the ZSM-5 catalyst.
2.3. Pyrolysis Process

A tubular furnace was used for pyrolysis at 700 °C with a heating rate of 25 °C/min, while the inert atmosphere was achieved by nitrogen flows (2.5 dm³/h). The layout of the pyrolysis process is shown in Figure 2.

During pyrolysis, 5 g of raw materials and 2.5 g of the catalysts were tested in separated form. The reaction time was 20 min at the set temperature (pyrolysis reactions were finished within 20 min). The plastic waste raw material and the catalyst were put into the reactor when the temperature was at a constant 700 °C. After a 20 min reaction time, the reactor was cooled to 150 °C by constant nitrogen flow (2.5 dm³/h) for 1 h. For condensation of the volatiles, a cryostat was used, then gases were collected into a Tedlar bag and analyzed. Pyrolysis oil was also collected in a small sample holder and further analyzed by gas-chromatography.
2.4. Product Analysis

A GC-FID (DANI GC (Rtx PONA (100 m × 0.25 mm, surface thickness of 0.5 µm) and Rtx-5 PONA (100 m × 0.25 mm, surface thickness of 1 µm) columns)) was used for the analysis of hydrocarbon composition of gases, while a GC-TCD (Gas Chromatography-Thermal Conductivity Detector) (Shimadzu GC-2010 (Carboxen TM 1006 PLOT column (30 m × 0.53 mm))) instrument was applied for the analysis of hydrogen, CO and CO₂.

Pyrolysis oil was dissolved in CS₂, then analyzed by GC-FID (DANI GC), using Rtx 1 dimetil-polysiloxan capillary column (30 m × 0.53 mm, thickens of 0.25 µm).

3. Results

3.1. Product Yields

The product yields from the decomposition of waste plastics mixture in relation to Me/Ni ratio are shown in Figure 3. The product yield was calculated on a weight basis. The yield of pyrolysis oil (Y_{po}) and char (Y_{c}) was measured based on the weight difference before and after the experiments. The amount of coke deposition on the catalyst surface was measured as following (1):

\[ Y_{cd} = \frac{m_0 - m_{i}}{m_0} \times 100 \]  

where the “m₀” is the initial weight of the catalyst with coke deposition, “mᵢ” is the weight of the catalyst after the treating at 800 °C in air for 1h. The gas yield (Y_{g}) was calculated by the following Equation (2):

\[ Y_{g} = 100 - Y_{po} - Y_{c} - Y_{cd} \] 

Figure 3. Product yields using different metal/catalyst ratios: (a) gases; (b) pyrolysis oil; (c) char; (d) carbon deposition.
The data show that gases’ fraction over the different catalyst with various Me/Ni ratio were higher compared to other products (liquid and char). This phenomenon was the consequence of high pyrolysis temperature (700 °C), which resulted in more gasification reactions. Regarding the influence of Me/Ni ratio, the gas yield decreased with increasing concentrations of the second metal. The highest gas yields were obtained with Ce, La and Mn catalysts at 0.1 Me/Ni ratios, which were 55.3%, 56.4% and 55.4% respectively. The data indicate that incorporating Ce, La and Mn resulted in the highest gas yields at lower ratios. In contrast, yields of pyrolysis oil increased by increasing the concentration of the second metal content; a ratio of 2.0 yielded the maximum pyrolysis oil (19.8%). At the same time, the amount of char and carbon deposited on the catalyst surface increased by increasing the content of the second metal, which explains decreasing gas yields (47.1%) at high ratios (2.0). Similar results were reported by Uemichi et al. [26] for the decomposition of polyethylene. They found that introducing promoters to catalysts resulted in more carbon deposition on the catalyst surface. Additionally, Khobragade et al. [27] studied the effect of promoters potassium and ceria on the performance of Co/SiO₂ catalysts for liquid fuel production from syngas. They also reported that higher promoter ratios can reduce surface area and pore volumes as a result of pore blockage. Though the Ca catalyst can promote, the Ce catalyst reduced coke formation on the catalyst, especially using a 0.1 Me:Ni ratio. The carbon deposition on the catalyst surface was 10.1% (0.1 Me/Ni ratio), 12.5% (0.5 Me/Ni ratio) and 15.2% (2.0 Me/Ni ratio) in case of Ce/Ni/ZSM-5, while that of Ca/Ni/ZSM-5 was 14.6% (0.1 Me/Ni ratio), 15.8% (0.5 Me/Ni ratio) and 17.6% (2.0 Me/Ni ratio).

3.2. Gases

The gas compositions are shown in Figures 4 and 5. The main composition of product gases was hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), linear and branched hydrocarbons (C₂-C₅).

![Graph showing product yields using different metal/catalyst ratios](image1)

![Graph showing gas yields over different metal/catalyst ratios](image2)

Fire 4. Gas yields over different metal/catalyst ratios: (a) hydrogen; (b) carbon monoxide.

The data show that the maximum syngas yield was with a 0.5 Me:Ni ratio. Ce/Ni/ZSM-5 and La/Ni/ZSM-5 had the highest yields of syngas among the other catalysts, which were 69.8 and 66.4 mmol/g, respectively. Regarding hydrogen production, Ce and La had the most advantageous effect because they increased the hydrogen yield significantly. For example, maximum hydrogen production (49.2 mmol/g) was obtained in the presence of a cerium catalyst while increasing the promoter content from 0.1 to 0.5 ratio, but thereafter, hydrogen content decreased with increasing Me concentration. This is in agreement with results obtained by Wu and Williams [28]. They concluded that increasing CeO₂ content for Ni/CoO₂/ZSM-5 catalysts leads to decreasing hydrogen concentration in the gas product from pyrolysis of polypropylene. The beneficial effects of cerium and lanthanum on synthesis gas yield are well known. However, there are few references to the combined use of Ce or La with nickel. As the morphological characteristics of the catalysts differed only slightly, the increase in hydrogen yield in our case was due to the synergistic effects of Ce and Ni, as well as those of La and Ni. Saad and Williams reported similar results in the case of pyrolysis of various wastes. The Co incorporation into the structure of Ni/Al₂O₃ had the advantageous properties for increasing syngas
yield [7]. Akubo et al. [29] also reported that hydrogen concentration in the gas product from pyrolysis of polyethylene plastic was enhanced by the addition of promoters to the Y-zeolite catalyst. On the other hand, the highest yield of carbon monoxide was achieved at the lowest Me content (0.1), which then decreased with increasing metal ratio. It was an important observation that the change in CO concentration was less than that of hydrogen. Regarding other gas compositions, the concentration of CH₄ was almost the same (9%–11%) for all catalyst types at 0.1 and 0.5 ratios, then decreased slightly (7.9%) with a 2.0 metal/catalyst ratio.

In this study, Ni/ZSM-5 catalysts with different promoter contents were synthesized in view of the applicability of catalysts and their regenerability. Regeneration of catalysts is necessary, mainly due to morphological changes caused by coke forming on its surface and subsequent decrease in activity. The incorporation of a second metal into the catalyst structure can support the higher decomposition of polymer main chain.

3.3. Pyrolysis Oil

Figure 6 shows the composition of the hydrocarbon content in the oil product from municipal plastic waste pyrolysis (HDPE, LDPE, PP and PET) over different catalysts with different promoters.

The concentration of C₅-hydrocarbons was significantly affected by the second metals and the Me/Ni ratio. Increasing the metal ratio in the catalyst content resulted in a clear increase of cyclic and non-branched hydrocarbons in the gas composition. In contrast, the concentration of branched hydrocarbons decreased from 29.2% to 21.8% with increasing the metal ratio, as the high metal content blocked the active sites of the catalyst that are responsible for isomerization reactions. In general, the incorporation of a second metal into the catalyst structure can support the higher decomposition of polymer main chain.
The results obtained from GC-FID analysis indicate that the oil product contained n-alkanes, n-alkenes, oxygenated compounds and single and multi-aromatic rings. Pyrolysis oils contain vast amounts of oxygen-containing hydrocarbons such as aldehydes, ketones, alcohols, carboxylic acids or even phenol and its derivatives. The data also show that no significant change was found in the composition of n-alkanes and n-alkenes by changing the Me:Ni ratio from 0.1 to 2.0. However, the concentration of n-alkanes and n-alkenes in the produced oil was in the range of 24.5%–28.4%. Increasing the second metal ratio in the catalyst led to a decrease in the concentration of oxygenated compounds from 35.5% to 27.7%. The tested metals had a significant effect on the concentration of aromatic hydrocarbons and, owing to in situ hydrogenation, on the ratio of n-paraffin/n-olefins. Regarding the influence of Me:Ni ratios on multi-ring aromatic compounds, the data show that increasing Me content resulted in a decrease of multi-ring aromatic compounds in the oil yields, from 7.5%–9.1% to 5.6–6.1%. On the other hand, a clear increase was observed in the concentration of single aromatic rings (19.2%) over Mg/Ni/ZSM-5 with the ratio of 2.0. According to the literature, many studies report that the aromatic content of oil products from catalytic pyrolysis are due to the presence of zeolite, which induces aromatization reactions [30,31].

4. Conclusions

In this study, Ni/ZSM-5 catalysts with different promoter contents were synthesized in view of enhancing the production of syngas from pyrolysis of real plastic waste mixture (mainly LDPE, HDPE, PP and PET) at 700 °C. The effects of the catalysts’ Me/Ni ratios on the pyrolysis product were studied. The results demonstrate that higher yields of gases may be obtained using metal-loaded catalysts than without them. The ratio of two metals did not significantly affect the yield of volatiles. In general, the incorporation of a second metal into a catalyst’s structure can support the lower decomposition of polymer main chains. Regarding Me:Ni ratios: in general, cerium, lanthanum and magnesium showed better performance at a 0.5 ratio. On the other hand, 2.0 Mg:Ni and Mn:Ni ratios showed better properties than others. Hydrogen yield could be especially increased, and higher yields of gaseous hydrocarbons were measured. However, little difference was observed between ratios of 0.5 and 2.0. A ratio of 0.5 Me:Ni was the best among all other ratios in terms of syngas and hydrogen production, and the maximum syngas yield was obtained using the Ce/Ni/ZSM-5 catalyst. However, raising the concentration of second promoters resulted in more coke formation on the catalyst surface, which leads to active site blockage. Long-term applicability is an important issue for Me/Ni/ZSM-5 catalysts. Further research work could continue with the investigation of the long-term applicability of catalysts and their regenerability. Regeneration of catalysts is necessary, mainly due to morphological changes caused by coke forming on its surface and subsequent decrease in activity.

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