9th Eco-Energy and Materials Science and Engineering Symposium

Improving Light Olefins and Light Oil Production Using Ru/MCM-48 in Catalytic Pyrolysis of Waste Tire

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Abstract

Mobil Composition of Matter (MCM) is the name given for a series of mesoporous materials. The MCM-48 is one of three phases of the mesoporous materials, which is cubic crystalline structure. The MCM-48 in this work was synthesized from silatrane route, and Ru metal was loaded by incipient wetness impregnation. This work investigated the activity and selectivity of MCM-48 and Ru/MCM-48 used as the catalysts for waste tire pyrolysis. The results showed that Ru/MCM-48 improved the gas yield. In addition, the use of Ru/MCM-48 catalyst produced light olefins twice as much as the non-catalytic pyrolysis. On the other hand, the catalyst helped to improve the oil quality by increasing light oil portion. Furthermore, it also reduced poly- and polar-aromatic compounds and sulfur content in the derived oil. Surface area analysis, XRD, and CHNS analysis were performed to explain the experimental results.

1. Introduction

Tires are non-biodegradable materials resulting in many problems such as landfill, hazardous, and environmental problems. Pyrolysis is an effective choice to manage the waste tire problem. It is a thermal decomposition of large molecular weight molecules to lower molecular weight products in the absence of

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oxygen. In general, the products of tire pyrolysis can be separated into liquid, gas and solid char. The light olefins are one of the fractions in the gas product from the pyrolysis of waste tire. They can be used as petrochemical feedstock and raw material of plastic industry. The use of catalyst can improve the quality of the product from pyrolysis. Ru/MCM-41 has been found to increase the gas yield (light olefins) due to its high cracking and dehydrogenating activity [1]. In 2008, Basagiannis and Verykios [2] studied the influence of the carrier on the steam reforming of acetic acid over Ru-based catalysts. They found that Ru can help increase the catalytic activity toward lower temperatures and higher hydrogen production rates. Moreover, Ru/HMOR can produce the high amount of light olefins and gas yield as studied by Dũng *et al.,* [1]. Later, it was found that 0.7% Ru supported HMOR can provide the highest light olefins yield [3]. Furthermore, the use of Ru/MCM-41 in the catalytic pyrolysis can produce 4 times higher light olefins yield than the non-catalytic case [1].

In particular, Mobil Composition of Matter (MCM) is the name given for a series of mesoporous materials that were first synthesized in 1992. The MCM-48 is a one of three phases of mesoporous MCMs which are MCM-41(hexagonal), MCM-48 (cubic), and MCM-50 (lamellar). The MCM-48 used in this work is the cubic mesoporous hydroxylated silicate, which consists of sub-micron-sized crystallites [4]. Since it is a mesoporous material that is in the same series of MCM-41, whose pore size has been proven appropriate to crack large moleculs of HCs and preserve light olefins formation, MCM-48 might have high potential to be used as a support for light olefins production as well. Consequently, 0.7%wt ruthenium metal supported on MCM-48 was used as a catalyst for potentially producing light olefins from waste tire pyrolysis.

2. Experimental Setup

2.1. Catalyst preparation

The silica MCM-48 was synthesized by silatrane route. Silatrane was first synthesized using the method of Wongkasemjit's group [5]. Silatrane precursor was added to hexadecyltrimethyl ammonium bromide (CTAB, purchased from Sigma Chemical Co.), and sodium hydroxide (NaOH, sigma Chemical Co.). After that, water was added with vigorous stirring, and gel was kept in an autoclave 16 hr at 140°C. The obtained crude product was filtered and washed with water to keep a white solid. The ratio of chemicals: $Si/CTAB/NaOH/H_2O$ was 1:0.3:0.5:62. Next, the white solid was dried at room temperature and calcined at 550 °C for 6 hours with the ramping rate of 0.5°C/min to obtain mesoporous MCM-48. For the Ru metal loading, the precursor solution of ruthenium (III) chloride hydrate was dropped on the support using the impregnation technique. The 0.7%Ru was loaded to 5 g. of the support, which needed 0.0719 g of $RuCl_3$. After that, the wet support was dried in an oven at 110°C for 3 hours and calcined in a furnace at 500°C for 3 hours with the heating rate of 10°C/min to obtain the catalysts in an oxide form. Then, the catalyst was reduced with H_2 at 400°C for 1-2 hours in order to convert the metal oxide form to metal element.

$$RuO_2 + H_2 \longrightarrow Ru + H_2O \tag{1}$$

2.2. Catalyst Characterization

The crystalline phase of the catalysts was examined using the X-ray diffraction pattern. X-ray diffraction (XRD) patterns were taken by using a Rigaku, Rint X-Ray diffractometer system (RINT 2200)

with Cu tube for generating CuKα radiation (1.5406 Å) and nickel filter. In this experiment, XRD determines the structure of catalysts and crystal size on the supports. A catalyst sample was ground to be fine and homogeneous particles, and then packed in a glass specimen holder. The data from XRD were analyzed and recorded by an on-line computer at the scanning speed of 0.5° min-1 and 2θ from 2° to 90°. The surface area, pore volume, and pore size of the studied catalysts were determined by N_2 physical adsorption with the Sorptomatic 2900 instrument. The percentage composition of sulfur in oil products and sulfur deposition on the spent catalysts were performed by using a LECO® Elemental Analyzer (TruSpec®S). The oil product of 0.1–1 g was absorbed on an aid support, which was put in a ceramic boat. The analyzed temperature of sulfur furnace was 1,350 °C.

2.3. Pyrolysis of Waste Tire

10 gram of waste tire sample was loaded, and was pyrolyzed at 500ºC in the lower zone of the pyrolysis reactor as in [6]. 2.5 gram of catalyst was packed and heated at 350 °C in the upper zone. The pyrolysis product was carried by a nitrogen flow, and was swept to the condensers. The non-condensable product was passed through the condensers and collected in the gas sampling bag. The solid and liquid products were weighed to determine the gas quantity by mass balance. The gas product was analyzed by a Gas Chromatography; Agilent Technologies 6890 Network GC system. The oil product was separated into maltene and asphaltene by adding n-pentane into the pyrolytic oil at the ratio of 40:1. Then, the maltenes were fractionated into saturated hydrocarbons, mono-, di-, poly-, and polar-aromatics by liquid adsorption chromatography [4].

3. Results and Discussion

MCM-48 is a mesoporous material, which has the 3D pore structure. The XRD patterns of synthesized MCM-48 and Ru-supported MCM-48 are presented in Fig.1. Only one peak of the both samples is detected at 2θ = 2.2°, which is the unique peak. The peaks corresponding of Ru metal are generally obtained at 38°, 42°, 44°, and 58° [7]. However, they are rarely detected because of low amount of Ru loading (0.7%wt). The loaded ruthenium metal does not affect the crystal structure.

The physical properties of fresh catalysts are shown in Table 1. The BET surface area and B.J.H. pore volume of the synthesized MCM-48 are 1,405 m^2/g and 0.87 cm^3/g, respectively. Moreover, the average pore diameter of synthesized MCM-48 is 35.9 Å. The covering of Ru metal causes the dramatic reduction in the surface area. In addition, the reduction of pore volume and pore diameter is caused by Ru metal, which covers the pore of synthesized MCM-48.

Table 1. Physical properties of studied catalysts.

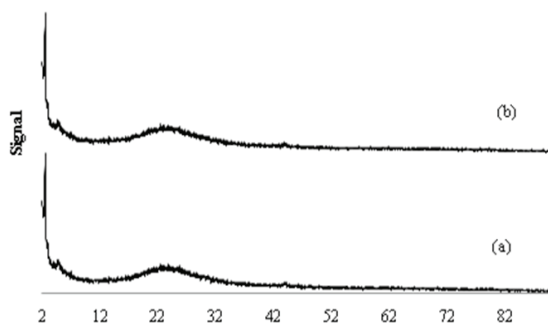|	Surface area (m^2/g)*	Pore volume (cm^3/g)**	Pore diameter (Å)**
MCM-48	1,405	0.87	35.87
0.7% Ru/MCM-48	915.7	0.63	32.94

*BET method, **B.J.H. method

Fig. 1. XRD pattern of catalysts: (a) MCM-48; and (b) 0.7%Ru/MCM-48.

3.1. Pyrolysis Products

According to Fig.2, the non-catalytic pyrolysis can produce the yield of gas, oil, and solid char of approximately 13%, 40%, and 47%, respectively. The use of MCM-48 can produce the gas yield of about 23%, and its production is higher than the non-catalytic case by 10%. Furthermore, Ru metal loading on MCM-48 also improves the gas production by 3% higher than the MCM-48 case. Moreover, the synthesized MCM-48 and Ru/MCM-48 decrease the oil production. They can produce less oil than the non-catalytic case by 7%, and 8%, respectively. MCM-48 was synthesized by silatrane route; therefore, it is not an acidic material. However, the effect on gas production of synthesized MCM-48 is through the 3D pore structure [8], which holds up the reactants inside at a long enough time that hydrocarbons have great mass transfer to undergo cracking reaction in the porous MCM-48. Moreover, the acidity of synthesized MCM-48 is less than other acidic zeolites such as HMOR, and HBeta; therefore, it has the low amount of coke deposition. The activity of catalyst is maintained because of the low amount of coke deposition [9]. Furthermore, the Ru loading on the MCM-48 increases the gas production. Ru metal, providing the metal sites, promotes the hydrogenation reaction of aromatic hydrocarbons, which are subsequently cracked and undergo ring-opening reaction in the pore of MCM-48.
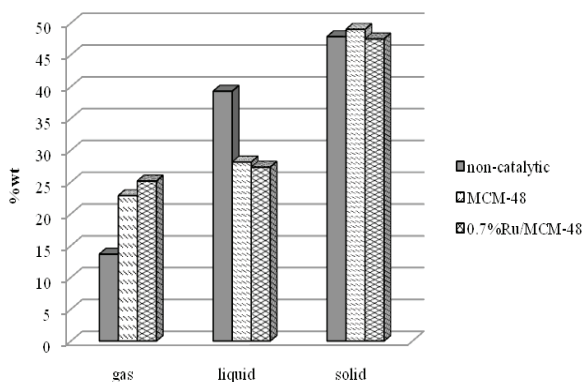

Fig. 2. Product distribution of pyrolysis products from using 0.7% Ru/MCM-48 catalysts.

3.2. Gaseous Products

The gas obtained from tire pyrolysis are, in general, composed of methane, ethylene, ethane, propylene, propane, C4-, C5-, and some traces of C6-, C7-, and C8-hydrocarbons. It was found that the gas also consisted of 0.233% H_2, and 0.423% CO_x for the non-catalytic case [10]. Fig.3. shows the composition of pyrolytic gas obtained from this work. The use of synthesized MCM-48 can drastically improve methane, ethane, and especially C4-, and C5-hydrocarbons. The C4- and C5-hydrocarbons productions are high in the gas because the tire is originally made from some butadiene and isoprene; hence, hydrocarbons chains tend to be cracked to the monomers. Moreover, the increment of C5-hydrocarbon might be resulted from the 3D pore structure of MCM-48, which holds up hydrocarbon molecules, then allowing some small gas molecules combine to larger gas molecules. Ru loaded catalyst produces the same gas yields as those of the MCM-48, except that of C5-hydrocarbons. Ru/MCM-48 can produce the significantly high amount of C5-hydrocarbons as compared to that of the other gases. It was reported that Ru metal can crack heavy hydrocarbons to gas products [11]. The increment of C5-HCs shown in the result consequently occurs from Ru metal that selectively cracks heavy HCs to C5s. According to Fig.4, MCM-48 and Ru/MCM-48 can produce high light olefins, which consist of ethylene and propylene in the gas. They can convert invaluable waste tire to valuable products at a high yield of light olefins. When Ru metal is loaded on MCM-48, the Ru/MCM-48 can improve the selectivity of light olefins. Due to the non-acidity of synthesized MCM-48, light olefins molecules can be preserved, because they are not further cracked to other HCs. Additionally, the meso-pore of MCM-48 gives higher selectivity of propylene than that of ethylene. With Ru metal, the yields of ethylene and propylene are slightly improved in conjunction with the higher gas production.
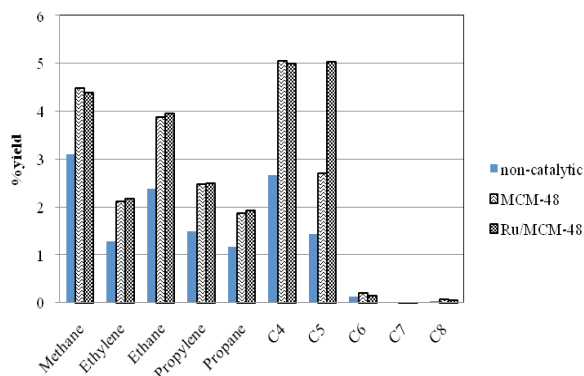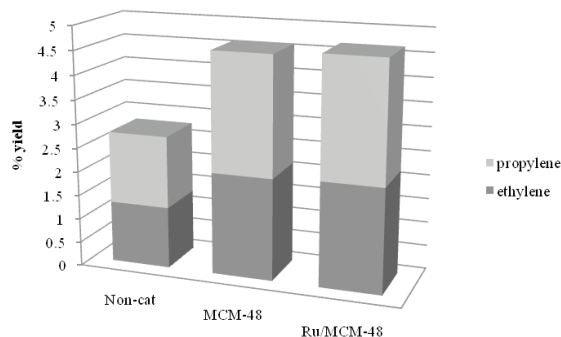

Fig. 3. Composition of pyrolytic gas.

Fig. 4. Light olefins production from using synthesized MCM-48 and Ru/MCM-48 catalysts.

3.3. Pyrolytic Oil

Furthermore, the catalysts can improve the quality of pyrolytic oils. As shown in Table 2, the amount of asphaltene is significantly reduced with using the synthesized MCM-48 and Ru/MCM-48. It can be seen that the MCM-48 has cracking ability; accordingly, the large HCs such as poly- and polar-aromatic can be cracked to smaller molecules. Thus, the MCM-48 dramatically reduces asphaltene. However, the Ru-loaded MCM-48 does not further reduce the amount of asphaltene as compared to the unloaded MCM-48; instead it slightly increases asphaltene.

In Fig.5, the molecular fractions, obtained from the liquid chromatography, in the oils indicate that the synthesized MCM-48 causes the increment of mono-, and di-aromatic HCs in accordance with decreasing saturated, poly-, and polar-aromatic HCs. As previously explained, the non-acidic MCM-48 has mild cracking activity with meso pore sizes, allowing large molecules to enter; thus, the amounts of poly- and polar-aromatics slightly decrease. In addition, saturated HCs are found decreasing as well. On the other hand, Ru loading on the MCM-48 support can dramatically improve saturated HCs in accordance with decreasing all aromatic compounds, indicating that Ru metal can promote high hydrogenation reaction. Consequently, multi-ring aromatics, especially poly- and polar-aromatic HCs, can be hydrogenated on the metal sites. Therefore, saturated HCs are increased at the expense of aromatic compounds from using the Ru/MCM-48 catalyst. Table 2 also shows that MCM-48 and Ru/MCM-48 insignificantly reduce the amount of sulfur in oil, because the sulfur slightly changes as compared to the non-catalytic case. This indicates the mild cracking activity of MCM-48 and the low activity of Ru on breaking C-S bonds in the pyrolytic oil. Due to the low C-S bond cracking activity, sulfur deposition on the spent catalysts is low as well.

Table 2. Amount of asphaltene in oil, sulfur deposition on spent catalysts, and sulfur in oils

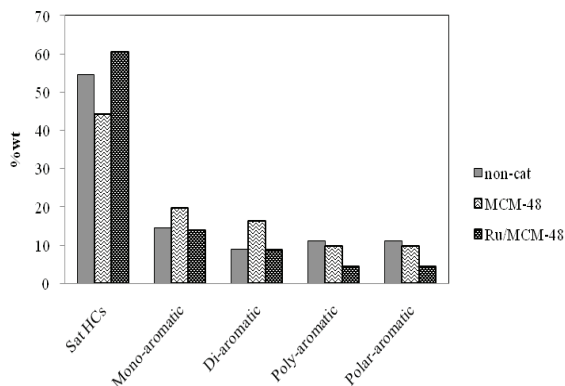|	%Asphaltene	%Sulfur deposition on spent catalysts	%Sulfur in oils
Non-catalytic	0.71	-	0.73
MCM-48	0.2	0.43	0.69
Ru/MCM-48	0.28	0.43	0.69

Fig. 5. Molecular compounds in oils from using synthesized MCM-48 and Ru/MCM-48 catalysts.

4. Results and Discussion

The catalytic pyrolysis of waste tire with using MCM-48 and 0.7% Ru/MCM-48 was performed in this work. The synthesized MCM-48 gave the dramatic improvement of gas production as compared to the non-catalytic case in accordance with decreasing the oil production, and Ru-supported MCM-48 also further increased the gas yield from using the pure MCM-48. Both MCM-48 and 0.7% Ru/MCM-48 enhanced the light olefins production. Furthermore, the catalysts can improve the quality of oil. Ru/MCM-48 gave the lighter oil as compared to the non-catalytic case. In particular, the maltene from using Ru/MCM-48 catalyst had the high concentration of saturated-hydrocarbons and low poly-, and polar-aromatic hydrocarbons.

The high activity and selectivity of Ru/MCM-48 is attributed to its mild cracking activity, preventing light olefins from over-cracking. The 3D pore structure of MCM-48 allowed high mass transfer, which improved overall reaction. Moreover, the Ru metal sites improved cracking and hydrogenation activities.

Acknowledgements

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