

CHAPTER V

ENHANCEMENT OF VALUABLE PETROCHEMICALS FORMATION IN WASTE TIRE- DERIVED OIL OVER 5 WT%NiKL

5.1 Abstract

A significantly-high concentration of mono-aromatics is commonly found in waste tire-derived oil. The important components of mono-aromatics are valuable chemicals such as ethylbenzene, toluene, mixed-xylenes, styrene, cumene and etc., which can be directly used as a petrochemical feedstock in refinery. Ni-doped KL zeolite was chosen as a catalyst, aiming to enhance the formation of valuable chemicals in tire-derived oil. The catalyst was characterized using BET, XRD, TGA, whereas GCxGC-TOF/MS and SIMDIST-GC were used for analysis of pyrolysis oil. As a results, the introduction of Ni on KL zeolite significantly increased mono-aromatics, olefins in the oil, whereas poly- and polar- aromatics drastically decreased. It clearly indicated that nickel on KL zeolite exhibited hydrogenation and ring-opening activities, which transformed multi-ring aromatics into mono-aromatics and olefins. Moreover, with Ni loading, the formation of ethylbenzene, cumene, and styrene was significantly enhanced in the tire-derived oil. The results indicated that the incorporation of nickel over KL zeolite led to selective conversion of bulky polycyclic aromatics into valuable chemicals.

5.2 Introduction

Petrochemicals can be classified into olefins and aromatics, and utilized as a raw material in manufacturing of plastics, solvents, detergents, synthetic rubber, cosmetic products and pharmaceuticals. From past to present, petrochemicals such as ethylene, propylene, butadiene and BTEX are mainly produced via cracking of naphtha and ethane derived from crude oil and natural gas (Ren *et al.*, 2009). However, the production of petrochemicals via petroleum and natural gas is not sustainable since the petroleum and natural gas resources continuously decrease. As a result, several alternative processes for production of petrochemical by utilization

of methane, coal, biomass and waste tire have attracted a great attention. Among these alternative processes, waste tire pyrolysis is considered as an effective process since it can eliminate waste tire problems by breaking up the tire molecules into valuable chemicals or fuel. Catalysts play an important role in conversion of tire molecules to valuable chemicals. Bi-functional catalysts have received much attention, especially in the improvement of waste tire-derived oil quality and valuable aromatics production since they provide interesting activities such as dehydrogenation/hydrogenation and ring-opening. Recently, Cu-doped on HY and HMOR zeolites enhanced the petrochemical selectivity in tire-derived oil. Cu/HY enhanced selectivity of benzene, ethylbenzene and cyclohexane, whereas Cu/HMOR strongly enhanced selectivity of ethylbenzene, toluene and xylenes (Yuwapornpanit, and Jitkarnka, 2015). The petrochemicals can be formed via hydrogenation and ring-opening of multi-ring aromatics or desulfurization of sulfur-containing compound in tire-derived oil. Nickel is one of transition metal, which is widely used in fluid catalytic cracking (FCC), cracking of bio-oil or biomass and desulfurization of fuels since nickel can provide dehydrogenation/hydrogenation and ring-opening activities (Maia *et al.*, 2010). Rodriguez-Castellón *et al.*, 2003 revealed that nickel supported on zirconium-doped mesoporous silica promoted the hydrogenation and ring-opening of tetralin. Furthermore, KL is a basic zeolite, and can be used as hydrogen storage material due to the hydrogen spillover activity. In addition, KL zeolite also exhibits dehydrogenation and aromatization activities (Smirniotis and Ruckenstein, 1995). Therefore, the combination of nickel and KL zeolite might promote the hydrogenation/dehydrogenation and ring-opening activity of catalysts, leading to the conversion of tire molecules to more valuable chemicals and lighter hydrocarbons products. The aim of this work was therefore to investigate the effect of nickel loading on KL zeolite on the species of waste-tire pyrolysis products, especially petrochemicals. Nickel was expected to promote the petrochemical formation in oil.

5.3 Experimental

5.3.1 Sample and Catalyst Preparation

A tire sample was prepared by shredding a waste tire, Bridgestone TURANZA GR-80. KL (500KOA, Si/Al=6, K-form) zeolite was purchased from TOSOH Corporation (Singapore), and calcined in standing air at 500 °C for 3 h (ramping rate of 10 °C/min). After that, nickel nitrate ((NiNO₃)₂•6H₂O) was impregnated in KL catalyst to obtain 5 %wt of atomic Ni loading. The impregnated KL were then dried overnight at 105 °C, and calcined at same condition as mentioned above. The catalyst powders were pelletized, crushed and sieved to 40-60 mesh of particle size. The Ni/KL catalyst was activated by reduction under hydrogen flow (30 ml/min) at 600 °C for 2 h (10 °C/min heating rate).

5.3.2 Catalyst Characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction (CuK α radiation), carried out in a Rikagu SmartLab X-Ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were recorded in the 5-65 °(2 θ) range using a scan speed of 10° (2 θ)/min. The surface area and pore volume of catalysts were measured using N₂ adsorption-desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument. The amount of coke deposition on the spent catalysts was measured by thermogravimetric analysis (TGA), carried out under flowing of nitrogen (10 ml/min) and oxygen (20 ml/min) on the Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The sample were heated up from room temperature to 900 °C with 10 °C/min ramping rate.

5.3.3 Waste Tire Pyrolysis

Pyrolysis apparatus was the same as the work of Yuwapompanit and Jitkarnka (2015). 30 g of shredded tire (20-40 mesh) was pyrolyzed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolytic products were carried by 30 ml/min of nitrogen flow to the catalytic bed packed with 7.5 g of catalyst and heated to 350 °C. After reached the desired ones, the temperatures of lower and upper zone were held for 2 h. The resulting products were separated into

5.3.4 Product Analysis

The liquid and solid products were weighed to determine the product yields. The gas yield was determined by mass balance. The gaseous products were analyzed by using GC, Agilent Technologies 6890 equipped with HP-PLOT Q column (300 mm x 0.32 mmID and 20 μm film thickness) and FID detector. The liquid products were dissolved in n-pentane (mass ratio of n-pentane/oil =40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μm). The maltene solution was then analyzed by Comprehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m x 0.25mmID x 0.25 μm) and the 2nd GC column was an Rxi®-17MS(1.790m x 0.1mmID x 0.1 μm). The primary column was held up at 50 °C for 2 min, and then heated up to 310 °C with a ramping rate of 5 °C/min. After final temperature was reached, it was held at 310 °C until the analysis was finished. For the secondary column, the column temperature was held at 60 °C for 2 min, and then ramped up to 320 °C with the ramping rate of 5 °C/min. After reached, the final temperature of column was held at 320 °C until the analysis was finished. The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography equipped with FID detector and a 15m x 0.25 mm x 0.25 μm WCOT fused silica capillary column. The petroleum fractions were cut based on their boiling point ranges according to the ASTM D2887; gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C).

5.4 Results and Discussion

5.4.1 Catalyst Characterization

The XRD patterns of the parent KL and the supported Ni catalysts are displayed in Figure 5.1. It can be clearly seen that both impregnated catalyst and parent KL clearly displayed the characteristic XRD pattern of LTL structure. Therefore, it can be concluded that the introduction of nickel on KL seems

not to affect the crystalline structure of KL. The peaks at $2\theta = 44.54^\circ$ and 52° indicate that the metallic nickel is present on the catalyst.

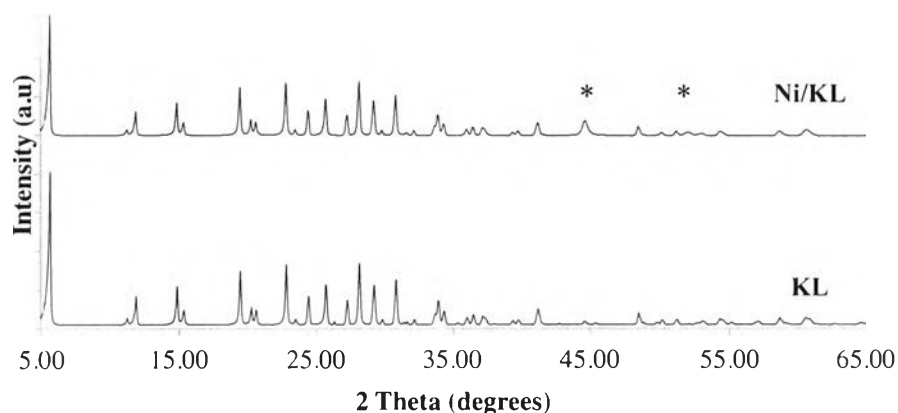


Figure 5.1 XRD patterns of KL zeolite and impregnated catalysts.

The BET specific area and pore volume of the parent KL and the supported Ni catalysts are displayed in Table 5.1. The addition of Ni to KL slightly decreases the surface area and micropore volume since some of nickel particles might be located at the internal pore of KL zeolite, and some metallic nickels may undergo sintering during the reduction of nickel oxide and then move to external surface of catalyst (Botas *et al.*, 2014).

Table 5.1 BET specific surface area and pore volume of catalysts

Catalyst	Surface Area (m ² /g)	Micropore Volume (cm ³ /g)
KL	218	0.113
Ni/KL	203	0.094

5.4.2 Pyrolysis Yields

The pyrolysis product distribution with parent KL and impregnated catalysts are displayed in Figure 5.2. It can be clearly seen that when metallic nickel was introduced on KL catalysts solid and liquid yields are lower than the parent KL, whereas the gas yield significantly increase. These results indicating that the incorporation of nickel over KL promotes cracking activity of KL. On the other, coke

formation over Ni/KL catalyst slightly decreases as compared to parent KL since the hydrogenation function of nickel might be favored on KL zeolite, so the formation of coke on spent Ni/KL slightly decreases.

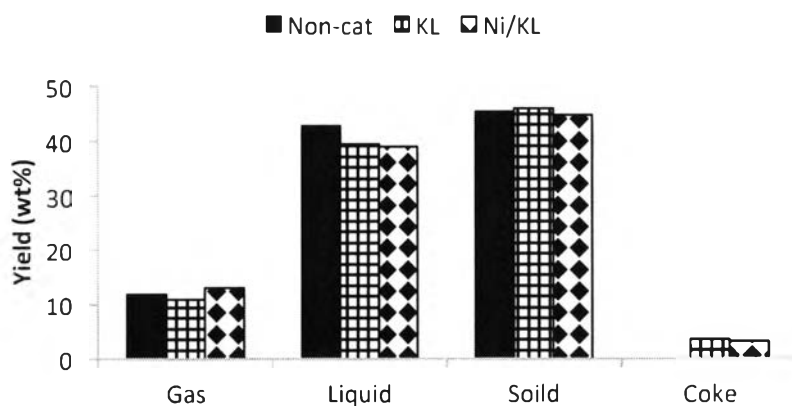


Figure 5.2. Effect of nickel loaded on KL on pyrolysis yields.

5.4.3 Waste Tire-derived Gas

KL zeolite does not significantly affect the gas products since the all composition in gas product quite similar to a non-catalytic case (see Figure 5.3). Slightly different is observed on the gas composition when doping with Ni. Ni/KL slightly increases the ethylene and propylene

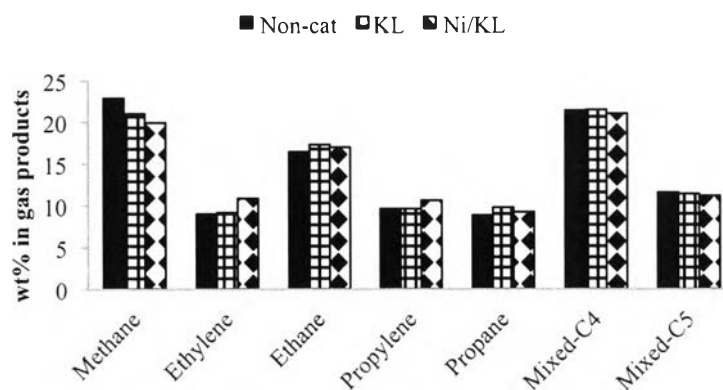


Figure 5.3. Effect of nickel loaded on KL on gas composition.

5.4.4 Waste Tire-derived Oil

KL zeolite enhances the gasoline and kerosene contents in oil, whereas the gas oil, LVGO and HVGO slightly decrease, indicating that a basic zeolite can promote cracking, which leads to high formation of lighter fractions (see Figure 5.4).

Furthermore, the increment of mono-aromatics and decrement of di-aromatics and naphthenes observed with the presence of KL catalyst also indicate the basic zeolite also promote cracking of di-aromatics and aromatization of naphthenes during waste tire pyrolysis. On the other hand, KL also enhances the amounts of poly- and polar aromatics. It can be explained that KL might promote the aromatization reaction via a base-catalyzing pathway, leading to the high formation of poly- and polar-aromatics.

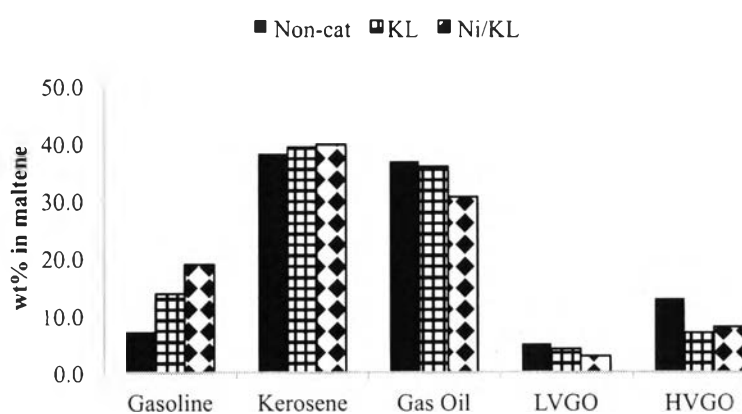


Figure 5.4. Effect of nickel loaded on KL on petroleum fractions in maltene.

In addition, the impregnation of KL on nickel strongly increases the production of gasoline and kerosene, but suppresses that of gas oil and LVGO. It is reasonable to conclude that the addition of nickel on the KL zeolite strongly promotes cracking of the two heavy fractions, leading to the formation of lighter fractions in oil. Furthermore, Figure 5.5 also shows that Ni/KL catalyst enhances the formation of olefins and mono-aromatics, while the formations of poly- and polar-aromatics drastically decrease. This result indicates that Ni species on KL zeolite promote hydrogenation and ring-opening of poly- and polar aromatics, resulting in the increment of mono-aromatics and olefins. However, maltenes obtained from KL and Ni/KL catalysts mainly consist of aromatics; therefore, they are quite not suitable for directly using as vehicle fuels. On the other hand, the main type of aromatics in maltenes is mono-aromatics, which mainly contains valuable chemicals such as ethylbenzene, toluene, styrene, xylenes, cumenes and etc. These chemicals can be

used as raw materials for production of polymers, detergents, synthetic fibers, and pharmaceuticals via refineries.

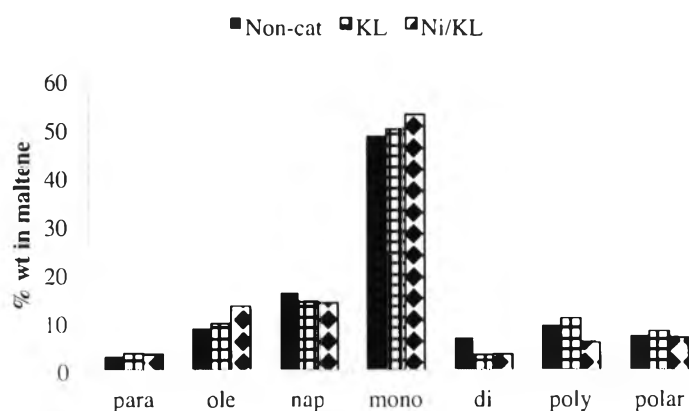


Figure 5.5. Effect of nickel loaded on KL on maltene composition.

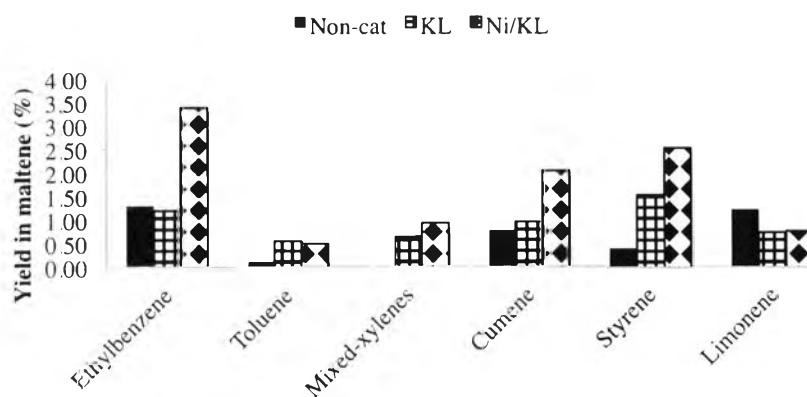


Figure 5.6 Yields of petrochemical in maltene obtained from Ni/KL

Figure 5.6 illustrates the yield of petrochemical in maltenes. As compared between catalytic and non-catalytic cases, KL and Ni/KL significantly decrease the formation of limonenes, whereas the formation of petrochemicals slightly increases since the limonene might transform to petrochemical species (Pines and Ryer, 1995). For KL catalyst, the formation of styrene, toluene, mixed-xylenes and cumene is slightly enhanced. This also indicates that the pore size and structure and basicity of KL catalyst can enhance the formation of valuable chemicals in maltene..

Furthermore, Ni-doped on KL strongly enhances the formation of ethylbenzene, mixed-xylenes, cumene and styrene since Ni might promote the

conversion of polycyclic aromatics to petrochemicals since Ni doping significantly reduced the concentrations of ethylbiphenyl, 4-isopropylbiphenyl, and methylphenanthrene in maltene by 50, 45 and 82 %, respectively. Ethylbiphenyl can be cracked to form ethylbenzene and benzene. However, the concentration of benzene in maltene is extremely lower than that of ethylbenzene, so the benzene radical might react with other hydrocarbon radicals to form other hydrocarbon species as displayed in Scheme 1. Cumene can be formed from cracking of 4-isopropylbiphenyl as displayed in Scheme 2. Benzene can also be a product of cracking of 4-isopropylbiphenyl, but it has not been found to increase, so it might convert to other hydrocarbon species via free radicals. Furthermore, methylphenanthrene can be hydrogenated at nickel sites, and then the carbon-carbon scission might firstly take place at the position (1), and then the carbon-carbon scission at the position (2) might take place, forming di-alkyl aromatics and alkyl-aromatics. If the radicals of di-alkyl- and alkyl-aromatics react with hydrogen, toluene and xylenes can be directly formed (see Scheme 3). However, the concentration of toluene has been found to decrease, so the toluene might be preferably converted to other hydrocarbons via free radicals.

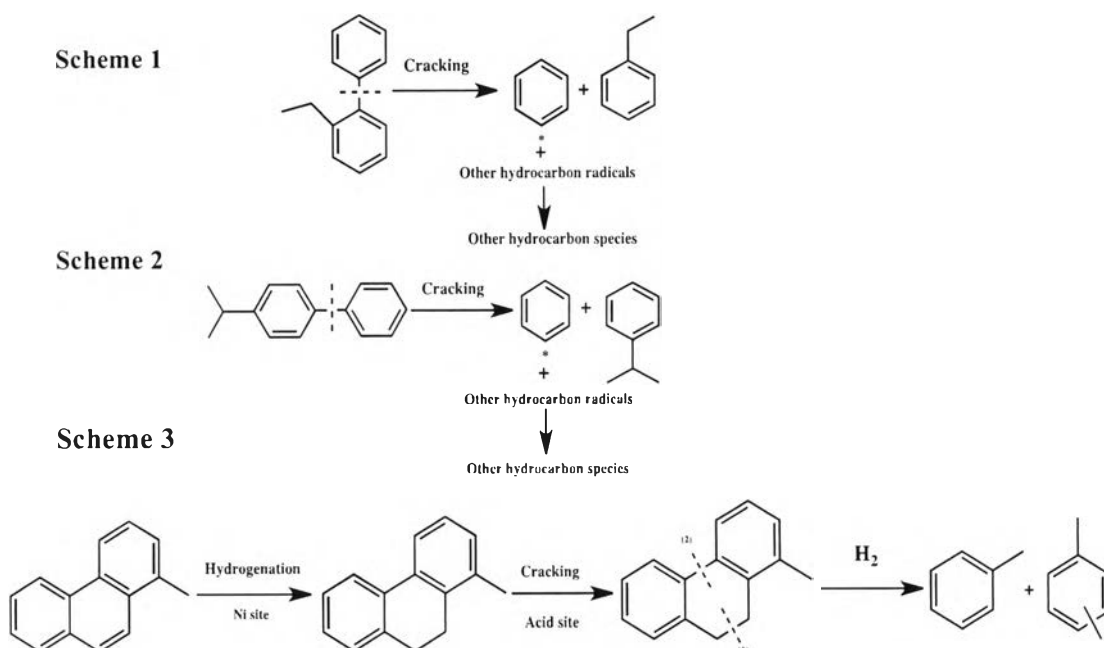


Figure 5.7 Possible reaction pathways for transformation of ethylbiphenyl, 4-isopropylbiphenyl and methylphenanthrene to valuable aromatics.

Table 5.2 also indicates that Ni/KL has a great potential in terms of petrochemical production, which provides a better petrochemical productivity than the KL zeolite. Therefore, Ni/KL catalyst is a promising catalyst for enhancement of petrochemical production in tire-derived oil.

Table 5.2 Petrochemical productivity

Catalyst	Petrochemical Productivity (Kg/ ton of tire)
Non catalytic case	11.0
KL	19.2
Ni/KL	36.5

5.5 Conclusions

Ni-doped KL zeolite can be considered as a promising catalyst for the enhancement of petrochemical formation in waste tire-derived oil via selective conversion of polycyclic aromatics to mono-aromatics. The incorporation of nickel on KL zeolite led to the formation of lighter hydrocarbons with a high proportion of gasoline, indicating that nickel species promote cracking activity of catalyst. Moreover, Ni/KL drove the conversion of polycyclic aromatics to petrochemicals, whereas parent KL catalyst enhanced the formation of mono- and poly-aromatics. The formation of ethylbenzene, xylenes, cumene, and styrene in waste tire-derived oil was significantly enhanced by Ni species. Moreover, with Ni doping, the petrochemical productivity from waste tire-derived oil increased roughly 1.5 times higher than that obtained from parent KL zeolite.

5.6 Acknowledgements

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5.7 References

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