

## CHAPTER VI

### ACID DENSITY AND ITS IMPACTS ON Zn-SUPPORT INTERACTION, TIRE-DERIVED OIL, PETROCHEMICALS, AND SULFUR REMOVAL

#### 6.1 Abstract

Over the past decades, many metals have been studied as promoters of zeolites for improving quality and quantity of pyrolysis products. Several research articles focused on the production of valuable products (fuels and petrochemical feedstock) and oil quality upgrading (the reduction of total aromatic content, the increment of saturated hydrocarbons, and sulfur reduction). Zinc is a metal that has been used in light alkane aromatization as catalysts, sulfur removal as adsorbents, and sintering resistance as promoters, for instances. For waste tire pyrolysis, zinc was thus expected to be a promoter of zeolites for production of petrochemical feedstock with a high content of commercially valuable mono-aromatics. Furthermore, sulfur content in tire-derived oils was expected to reduce as well. This work therefore studied the effects of zinc promoter and Zn-support interaction (Zn on HBETA, HY, and HMOR) on tire-derived oil, petrochemicals and sulfur removal. The results showed that zinc promoted gas yields and the production of small molecules in oils, indicating that zinc promoted cracking activity of zeolites. Furthermore, zinc was found to enhance the catalyst stability since zinc-promoted catalysts generated a lower amount of coke than their pure zeolites. Moreover, the promoted catalysts increased the concentrations of paraffins and mono-aromatics in conjunction with the decreases in other aromatic groups, indicating that zinc can promote hydrogenation, ring-opening and aromatization activities. Furthermore, sulfur content in oils was decreased in all zinc-supported catalysts, especially those in the groups of thiophenes, benzothiophenes, dibenzothiophenes and naphthothiophenes, indicating the sulfur removing activity of Zn promoter. The ability of sulfur removal from oils strongly depended on acid density of catalysts. Furthermore, it was found that Zn loaded on HBETA, HY and HMOR zeolites can produce high selectivity of cumene and ethylbenzene in gasoline. Moreover, Zn/HBETA highly produced cyclohexane while the other zinc-loaded catalysts also highly produced styrene.

## 6.2 Introduction

Pyrolysis of waste tire is an effective method for recovering the hydrocarbon substances that can be produced in forms of gas and liquid products. In terms of product applications, tire-derived oils have a potential to serve as liquid fuels and petrochemical feedstock. Several researchers studied the improvement of pyrolysis oil quality by enhancing light oil yields, petrochemical yields, and removing sulfur content. For examples, Qu *et al.* (2006) studied the catalytic co-pyrolysis of waste tire with lubricant base oil (LBO) using ZSM-5. They found that LBO can enhance the degradation rate of waste tire, and increase the amount of light oils as well. Dung et al (2009) studied the use of ITQ-21 as additives of HMOR zeolite in waste tire pyrolysis process. They found that the additives can promote kerosene and mono-aromatic productions. Furthermore, benzene, toluene and xylenes were also produced from the pyrolysis of waste tire using USY, Y and ZSM-5 as catalysts (Williams and Brindle, 2003; Boxiong *et al.*, 2007). However, the oils contain a high amount of sulfur because sulfur is an essential ingredient in tire production. So, the quality of tire-derived oils must be improved before the uses. The sulfur species in tire-derived oils were reported by William and Brotill 1995. They revealed that the sulfur-polycyclic aromatic hydrocarbon (PASH) species were benzothiophene, dibenzothiophene and their derivatives. These species are found in crude oil as well. So, the hydrotreating processes for petroleum-based oil can be also applicable for tire-derived oils. Several articles reported that the hydrodesulfurization of sulfur-containing compounds can produce valuable petrochemicals such as toluene, ethylbenzene, and styrene (Dumeignil *et al.*, 2005; Yao *et al.*, 2005) as co-products as well. The concentration of petrochemicals in tire-derived oils can be also improved via hydrodesulfurization. Since only a little quantity of valuable C<sub>6</sub>-C<sub>8</sub> petrochemicals can be produced via thermal pyrolysis, the enhancement of C<sub>6</sub>-C<sub>8</sub> compounds in tire-derived oil via desulfurization can be significant although there exists only a little amount of sulfur compounds in it (~1.4 wt%)

Zinc is a metal used as promoters for catalysts in many applications because it has several outstanding properties. For examples, zinc-loaded catalysts were used as aromatization catalysts for a light alkane feed stream (Berndt *et al.*, 1996;

Viswanadham *et al.*, 1996). Zinc-exchanged zeolites were used to remove sulfur-containing compounds from liquid fuels (Hernández-Maldonado *et al.*, 2005; Villarroel *et al.*, 2008; Oliveira *et al.*, 2009; Shangguan *et al.*, 2013). Furthermore, ZnO can limit the H<sub>2</sub>S poisoning of copper by forming ZnS that is more strongly favored thermodynamically than the Cu<sub>2</sub>S form at 500 K (Hassan *et al.*, 2008). Twigg and Spencer (2001) studied the deactivation of copper-loaded catalysts for hydrogenation reactions. They found that zinc can be used as a promoter of copper in the catalyst fields for improvement of stabilities (sulfur resistance, thermal sintering, etc.). For the waste tire pyrolysis, zinc is therefore a remarkable metal for use as a promoter of zeolites since it might improve quality of tire-derived oils in the terms of sulfur reduction, and simultaneously promote mono-aromatic formation as valuable petrochemicals.

Hence, this work studied on the existence of zinc-support interaction and its impacts on tire-derived oil, petrochemicals and sulfur removal. Zinc was loaded at 5 wt% on three types of supports (HBETA, HY and HMOR zeolites) using impregnation method. Pyrolysis oils were analyzed to determine their compositions and petroleum cuts by using GC×GC-TOF/MS and SIMDIST-GC, respectively. Gas products were analyzed their compositions by using GC-FID. All three pyrolysis products (gas, oil and char) and spent catalysts were analyzed and/or calculated sulfur distribution by using S-analyzer.

## 6.3 Experimental

### 6.3.1 Catalyst Preparation

Commercial zeolites, NH<sub>4</sub>-BETA, HY and HMOR, supplied by TOSOH Company (Singapore) were calcined in stagnant air at the condition shown in Table 6.1. The calcined zeolites were subsequently impregnated with an appropriate amount of a zinc solution (Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) to achieve the zinc loading of 5 wt%, dried overnight in an oven at 120 °C, and calcined again at the same calcination conditions. The calcined catalysts were then reduced at 500 °C for 2 hours in hydrogen environment. Finally, all catalysts were pelletized, crushed, and sieved into a particle size of 40-60 mesh.

### 6.3.2 Catalyst Characterization

The XRD patterns of catalysts were obtained from XRD machine (Rikagu) using CuK $\alpha$  radiation operated at 40 kV and 30 mA. The scanned angle was started from 5° to 65° with a scanning speed of 5°/min. Thermo Finnigan TPDRO 1100 was used to characterize metal-support interaction of the catalysts via comparison among temperature programmed reduction (TPR) profile under 4.99 % H<sub>2</sub>/N<sub>2</sub> flow at 20 ml/min with a heating rate of 20 °C/min from room temperature to 950 °C. XPS spectra were obtained by using an AXIS ULTRADLD (Kratos) to determine metal species in a catalyst. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated at the pass energy of 160 eV and 40 eV to acquire wide scan and core level spectra, respectively. All peaks were calibrated from referring C1s spectra (Binding energy = 284.6 eV). The amount of metal loading on zeolites was determined by using Atomic Absorption Spectrometer (Varian, SpecterAA 300 model) ULTRADLD. A sample was digested with an acid solution (1 conc. HCl: 1 conc. HF: 1 conc. H<sub>2</sub>O) to a solution of the metal element. Thermo Finnigan Sorptomatic 1990 equipment was used to determine BET surface area and pore volume of catalysts by N<sub>2</sub> physical adsorption. Thermogravimetric/Differential Thermal Analysis, TG/DTA (Perkin Elmer/Pyris Diamond), was used to determine the amount of coke deposited on spent catalysts with the heating rate of 10 °C/min from room temperature to 900 °C. Sulfur content on catalyst surface was acquired from LECO®Elemental Analyzer (TruSpec®S).

### 6.3.3 Waste Tire Pyrolysis

Pyrolysis apparatus was the same as the work of Dũng *et al.* (2009). The reactor was divided into two zones; the lower zone (pyrolysis zone) was loaded with 30 grams of shredded tire (20-40 mesh), and the upper zone (catalytic zone) was loaded with 7.5 grams of a catalyst. Two zones were heated from room temperature to 500 °C and 300 °C with a heating rate of 10 °C/min at atmospheric pressure, respectively, and the final temperatures were held at the target temperatures for 2 hr. High purity nitrogen was used as a carrier gas. The condensable products or oils were collected in the condensers immersed in an ice-salt (NaCl) bath. A gas sampling bag

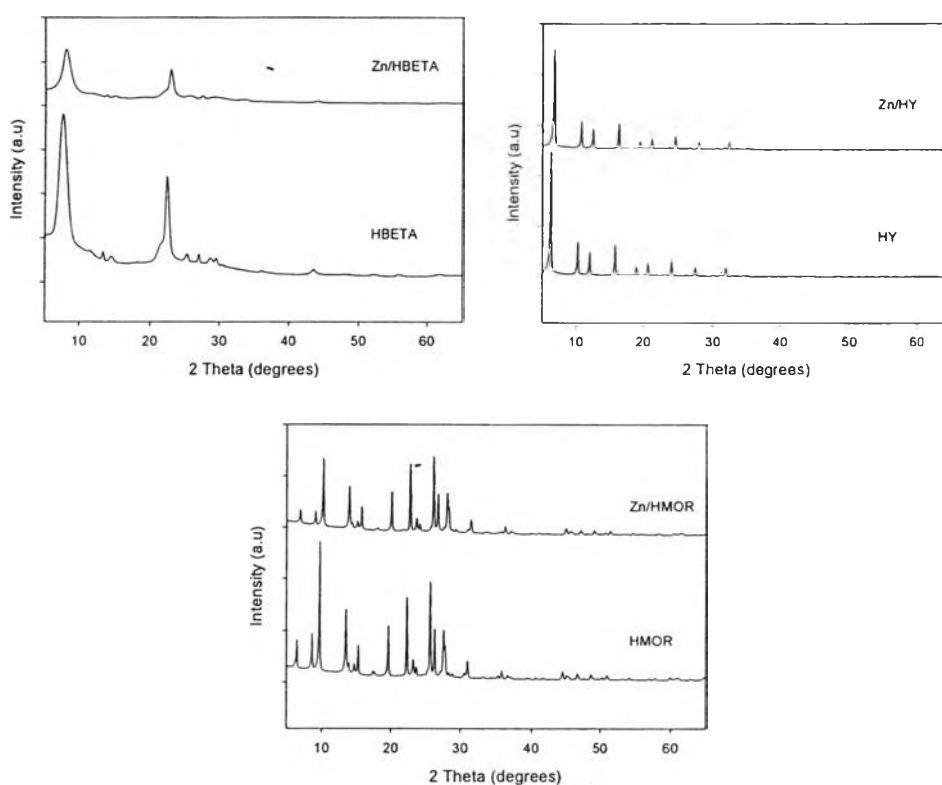
was used to collect uncondensable products or gas products, while solid products or chars remained in the bottom of the reactor.

**Table 6.1** Physical properties of zeolites and calcination condition of commercial zeolites before using as supports

	Si/Al ratio	Pore Structure	Calcination Temperature (°C)	Ramping Rate (°C/min)	Holding Time (hr)
BETA	13.5	3D	600	2	5
Y	7.5	3D	500	5	3
MOR	9.5	1D	500	5	3

The gas yields was calculated from mass balance, which equals to initial weight of tire abstracted by the liquid and solid yields, and the amount of coke on the catalyst surface determined from the TG/DTA instrument. Before analysis of oil products, asphaltene was first precipitated via mixing the oils with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1 for 18 hr. A Teflon membrane (0.45  $\mu\text{m}$ ) was used to filter the precipitated asphaltene. GC $\times$ GC-TOF/MS apparatus equipped an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator was used to analyzed oil compositions. The instrument was operated by the cooperation of two GC columns (Thames Restek, Sounderton, UK). The 1<sup>st</sup> GC column was a non-polar Rtx®-5Sil MS, 30 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu\text{m}$  film thickness. The 2<sup>nd</sup> GC column was an Rxi®-17 MS, 1.10 m  $\times$  0.10 mm ID  $\times$  0.10  $\mu\text{m}$  film thickness. Maltene solution samples were prepared by diluting 1  $\mu\text{L}$  of maltene with CS<sub>2</sub> into 2 mL, and analyzed by injection into the instrument via a splitless injector operated at 250 °C using 1.0 mL/min of helium as a carrier gas. Moreover, a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method was used to determine the true boiling point curves of maltene solutions. The equipment was installed with FID and WCOT fused silica capillary column, 15 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ . The true boiling point curves were next cut into

petroleum fractions according to their boiling points; 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). A GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 µm film thickness and 30 m × 0.32 mm ID) was used to determine the compositions and concentrations of the gas products. Furthermore, sulfur contents in the liquid and solid products were also determined by using a LECO®Elemental Analyzer (TruSpec®S) whereas the sulfur content in gas products was calculated via mass balance.



**Figure 6.1** XRD patterns of Zn-loaded catalysts.

## 6.4 Results and Discussion

### 6.4.1 Catalyst Characterization

The XRD patterns of zinc-promoted catalysts and their pure supports are shown in Figure 6.1. Obviously, it can be observed that the presence of zinc on

zeolites does not destroy zeolite structure. The  $2\theta$ s of  $36.5^\circ$ ,  $39.1^\circ$ ,  $43.5^\circ$  and  $54.6^\circ$  are the characteristic peaks of  $Zn^0$ , and the  $2\theta$  of  $31.8^\circ$ ,  $34.3^\circ$ ,  $36.5^\circ$ ,  $47.6^\circ$  and  $57.2^\circ$  are those of  $ZnO$ . However, the characteristic peaks of zinc species cannot be clearly seen since might be highly dispersed on their supports. Table 6.2 shows the surface area and pore volume of all catalysts. The introduction of zinc onto zeolites decreases both pore volume and BET specific surface area because zinc might partially block the pore of zeolites. The amounts of zinc loading and zinc species in each catalyst are shown in Table 6.3. In Figure 6.2, the XPS spectra ( $2p_{3/2}$ ) indicate that zinc species found on the catalysts are composed of a high amount of metallic Zn (82.2 wt%, 90.4 wt%, and 92.0 wt% for Zn/HBETA, Zn/HY, and Zn/HMOR, respectively) with a low amount of ZnO (17.8 wt%, 9.60 wt%, and 7.96 wt% for Zn/HBETA, Zn/HY, and Zn/HMOR, respectively). The melting point of metallic zinc is around  $419.5^\circ\text{C}$  (Perry, 2011), while the reduction temperatures of zinc-loaded catalysts are much higher (as observed from the TPR profiles in Figure 6.3) than the melting point. However, the catalysts can be reduced at  $500^\circ\text{C}$  as confirmed by XPS due to the Zn-support interaction and the dispersion of Zn clusters on the support. However, the metal loading of  $\sim 3$  wt% observed on all Cu-loaded catalysts, instead of the expected 5 wt% is attributed to the partial vaporization of Zn from the surfaces during the reduction.

**Table 6.2** BET surface area and pore volume of catalysts

Catalyst	BET surface area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{cm}^3/\text{g}$ ) <sup>*</sup>
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
Zn/HBETA	492	0.233
Zn/HY	515	0.259
Zn/HMOR	380	0.185

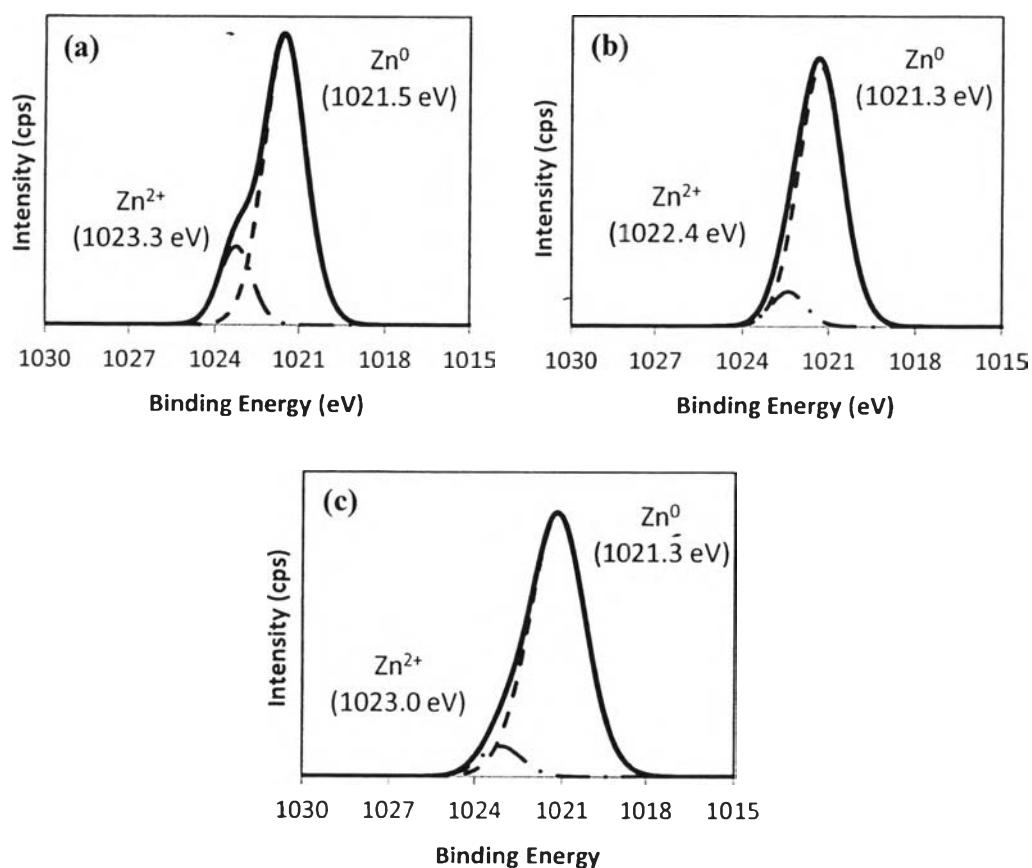
<sup>\*</sup> Horvath-Kawazoe (H-K) Calculations

**Table 6.3** Zinc content and species in catalysts

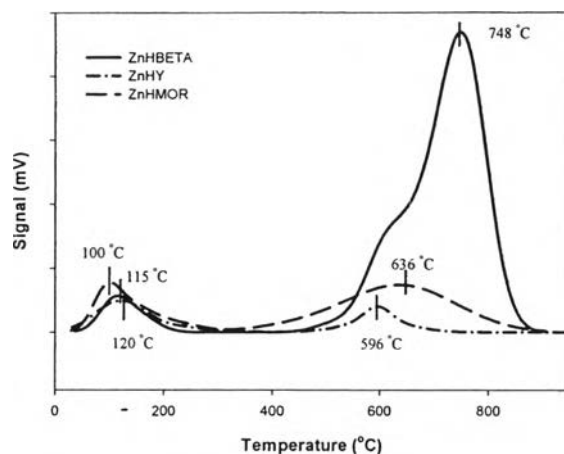
Catalyst	Zinc Content in Catalyst (wt%)*	Zinc Specie (wt%)/ Binding Energy (eV)**	
		Zn <sup>0</sup>	ZnO
Zn/HBETA	3.61	82.2/ 1021.5	17.8/ 1023.3
Zn/HY	3.04	90.4/ 1021.3	9.60/ 1022.4
Zn/HMOR	2.92	92.0/ 1021.3	7.96/ 1023.0 -

\* from Atomic Absorption Spectroscopy (AAS)

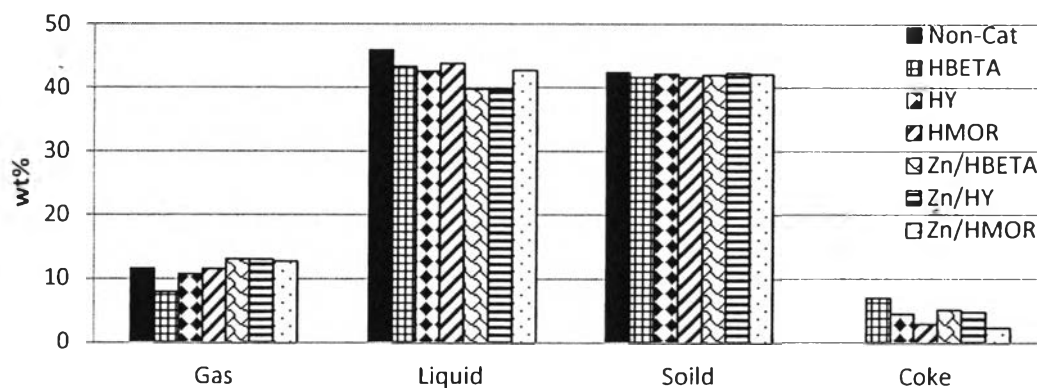
\*\* from X-Ray Photoelectron Spectroscopy (XPS)

**Figure 6.2** XPS spectra of zinc-loaded catalysts; (a) Zn/HBETA, (b) Zn/HY, and (c) Zn/HMOR.





**Figure 6.3** TPR profiles of Zn-loaded catalysts.



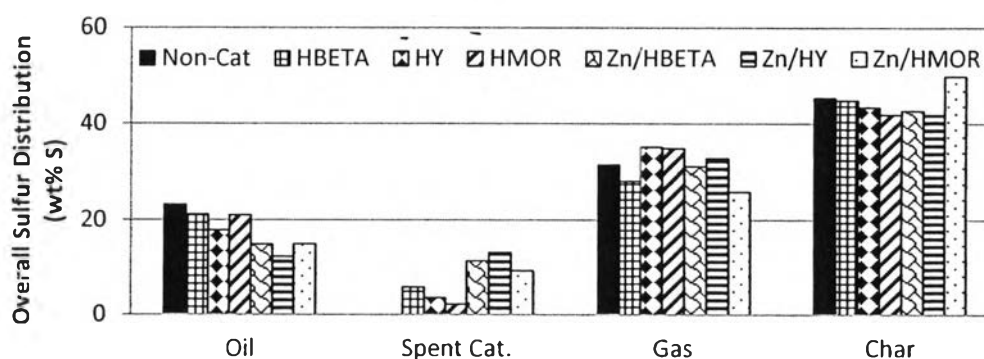
**Figure 6.4** Product distribution in Zn-loaded catalyst cases.

#### 6.4.2 Product Distribution

All zinc-loaded catalysts slightly increase gas production, and decrease liquid yields with an extent of coke formation and a constant solid yield as shown in Figure 6.4. It indicates that zinc slightly promotes the cracking activity of zeolites. Surprisingly, all zinc-promoted catalysts (except Zn/HY) reduce the amount of coke on the catalyst surfaces.

#### 6.4.3 Acid Density of Catalyst and Its Influence on Sulfur Removal from Pyrolysis Oils and Zn-Support Interaction

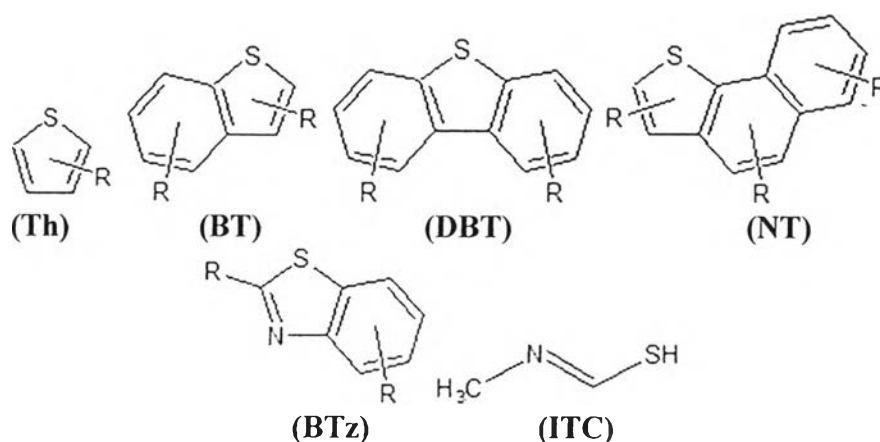
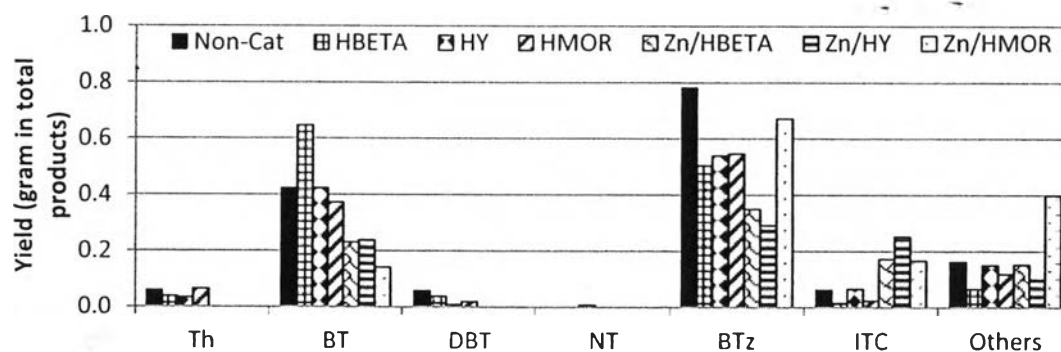
Figure 6.5 and Table 6.4 show that Zn/HY can remove sulfur from the tire-derived oil at the highest amount, followed by Zn/HMOR and then Zn/HBETA. It can be indicated that the sulfur removal ability of zinc strongly depends on the acid density (represented by the Si/Al ratios of Zn/HY, Zn/HMOR, and Zn/HBETA; that are, 7.5, 9.5, and 13.5, respectively). Since Zn can well interact with  $H^+$  on the zeolite supports, the acid sites promote the electron deficiency of zinc (Du *et al.*, 2005), resulting in higher adsorption strength between Zn and a sulfur-containing hydrocarbon, the easier C-S bond cleavage, and then the better S removal from the hydrocarbon. Furthermore, the acid density also affects the surface cleaning ability of Zn-loaded catalysts. The TPR profiles and binding energies of zinc-loaded catalysts (Figure 6.3 and Table 6.3, respectively) can indicate the Zn-support interaction of the zinc-loaded catalysts. It can be seen that the reduction temperature and  $2p_{3/2}$  binding energies (both  $Zn^0$  and ZnO) of Zn/HBETA are the highest, followed by those of Zn/HMOR and Zn/HY, indicating that the interaction between Zn-HBETA is the strongest, followed by that between Zn-HMOR and then Zn-HY. The results agree with the report of Du *et al.* (2005) that the sulfur tolerance can be improved by decreasing the sulfur-metal strength; thus, increasing the acid sites. Zn/HY with the lowest metal-support interaction can create the weakest Zn-S bonds, resulting in the highest surface cleaning ability. However, in this work it is difficult for the surface cleaning to occur because the Zn-S bond strength is so strong (Chianelli *et al.*, 2002), resulting in the higher desulfurization activity than the surface cleaning activity.



**Figure 6.5** Overall sulfur distribution in Zn-loaded catalyst cases.

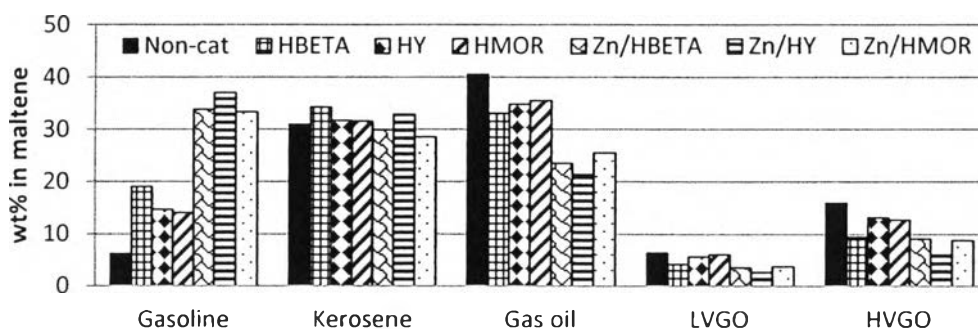
**Table 6.4** Sulfur content in oil (wt%)

Catalyst	Sulfur Content in oil (wt%)
No Catalyst	1.14
HBETA	1.10
HY	0.943
HMOR	1.08
Zn/HBETA	0.838
Zn/HY	0.691
Zn/HMOR	0.783

**Figure 6.6** Major sulfur-containing compounds in tire-derived oils.**Figure 6.7** Yield of sulfur-containing species.

In this work, the Zn/HY catalyst appears to be the best catalyst among all tested catalysts for sulfur removal from tire-derived oils.

Sulfur-containing compounds in oils can be classified into six groups: thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC) as shown in Figure 6.6. Figure 6.7 shows that Th, DBT and NT are totally reduced when zinc was loaded on all types of the zeolites because zinc can react with sulfur atoms in sulfur-containing compounds, and form thermodynamically stable ZnS (Twiggs and Spencer, 2001; Hassan *et al.*, 2008). Furthermore, BT is highly reduced in all Zn-loaded catalyst cases as compared with pure zeolite cases. It can be concluded that zinc can promote sulfur removal activity of zeolites.

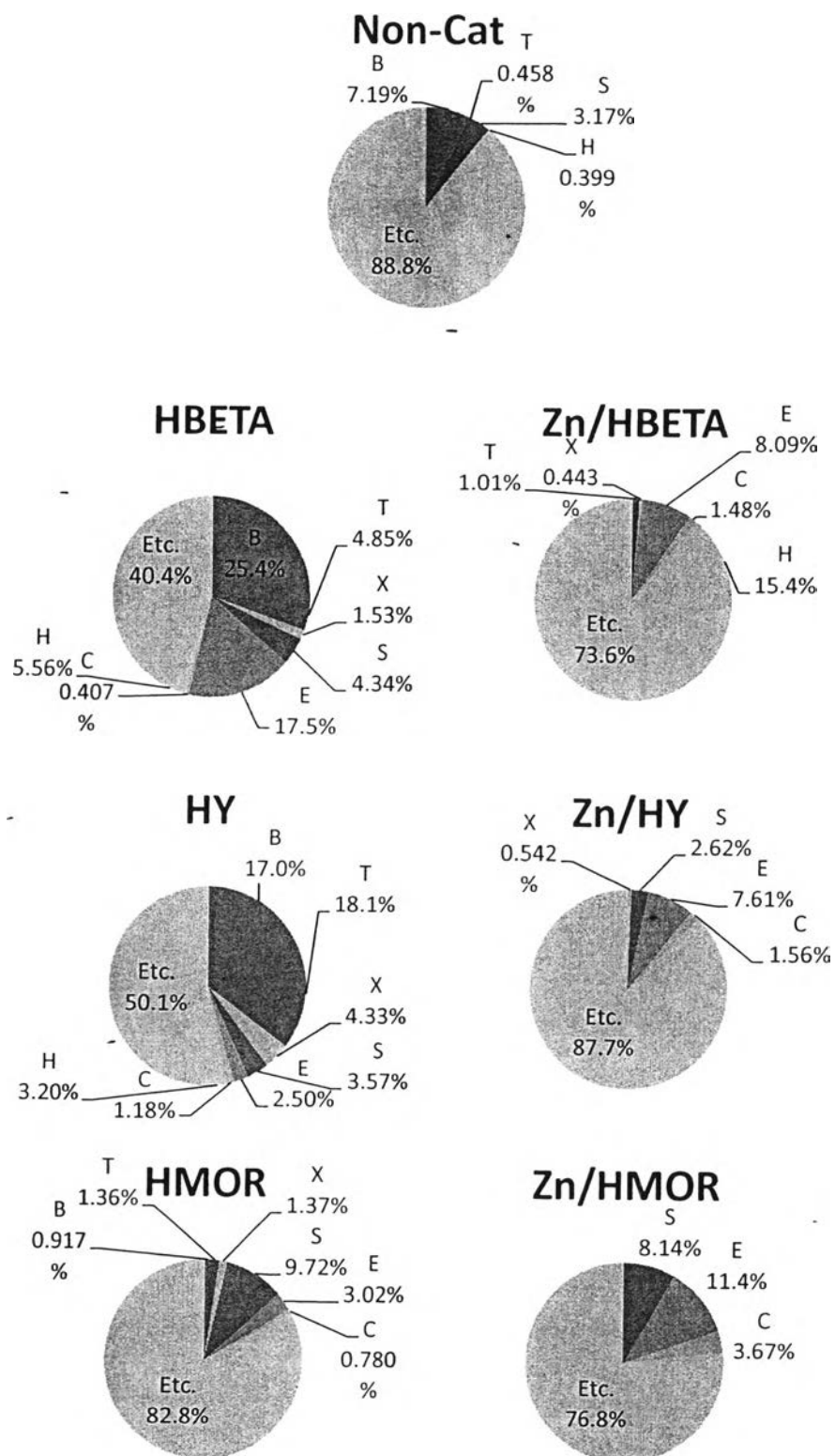


**Figure 6.8** Petroleum cuts of maltene in zinc-loaded catalyst cases.

**Table 6.5** Chemical composition in each petroleum cuts

	Gasoline	Kerosene	Gas Oil	LVGO	HVGO
Paraffins	0.00-26.1	0.468-1.66	3.95-23.6	0.00-13.5	0.00-32.6
Olefins	0.445-11.3	0.254-9.04	0.00-9.51	0.00-22.3	-
Naphthenes	3.77-39.1	1.86-13.0	0.00-16.8	0.00-22.0	-
Aromatics	60.0-96.2*	76.3-96.2	65.4-80.9	71.1-100	67.4-100

\* 37.5 – 77.4 wt% of mono-aromatics in gasoline



**Figure 6.9** Selectivity of petrochemicals in gasoline range products.

**Table 6.6** Petrochemicals productivity from waste tire pyrolysis

Catalyst	Petrochemical Productivity (kg/ton of tire)
No Catalyst	3.19
HBETA	49.1
HY	31.2
HMOR	10.6
Zn/HBETA	35.5
Zn/HY	18.2
Zn/HMOR	33.0

#### 6.4.4 Effect of Zinc-loaded Catalysts on Tire-derived Oils

Figure 6.8 shows that zinc can promote cracking activity of zeolites, resulting in the increment of gasoline fraction. Moreover, all petroleum cuts are mainly composed of aromatics (Table 6.5), indicating that the tire-derived oils are not suitable for direct use as fuels. However, Figure 6.9 shows that all zinc-loaded catalysts highly produce ethylbenzene and cumene. The catalysts (except Zn/HBETA) also highly produce styrene, while cyclohexane is highly produced by Zn/HBETA. However, the productivity of petrochemicals (Table 6.6) is reduced when zinc was loaded on the zeolites, except the Zn/HMOR case.

## 6.5 Conclusions

This work studied the effect of Zn-promoted catalysts on tire-derived oil, petrochemicals and sulfur removal by loading the metal on three types of supports with different Si/Al ratios (HY, HMOR, and HBETA with Si/Al = 7.5, 9.5, and 13.5, respectively). The acid density of Zn-promoted catalyst exhibits an important role on sulfur removal from pyrolysis oils. Sulfur content in oils was ranked in the order of: Zn/HY (0.691 wt%) < Zn/HMOR (0.783 wt%) < Zn/HBETA (0.838 wt%). All Zn-loaded catalysts can produce a high selectivity of cumene and ethylbenzene in

gasoline. Moreover, Zn/HBETA highly produced cyclohexane while the other zinc-loaded catalysts also highly produced styrene.

## 6.6 Acknowledgements

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