

CHAPTER V

EXISTENCE OF Cu-SUPPORT INTERACTION AND ITS IMPACTS ON TIRE-DERIVED OIL, PETROCHEMICALS, AND SULFUR REMOVAL

5.1 Abstract

Metal-loaded zeolites are potential catalysts for upgrading the quality and quantity of waste tire pyrolysis products. Since the catalysts can exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, aromatization, etc. that can be acquired from metal and zeolite properties. Copper is widely used in several applications such as selective hydrogenation of undesired unsaturated hydrocarbons in a mixed-C₄ stream, and sulfur removal from liquid fuels, etc. So, copper was expected to be a promoter of zeolites for enhancing the quality of tire-derived oils in terms of sulfur removal from oils and the increase in valuable petrochemicals in oils. This work thus studied the effect of copper-support interaction on tire-derived oils, petrochemicals, and sulfur removal using three types of zeolites (HBETA, HY and HMOR) as supports with a 5 wt% metal loading. Catalytic pyrolysis of waste tire was operated in a bench reactor, and GC×GC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products for their chemical compositions and petroleum fraction, respectively. Sulfur in the pyrolysis products was determined by using an S-analyzer, whereas the gas composition was analyzed by using a GC-FID. As a result, all copper-promoted catalysts can reduce more sulfur content in oils than their pure zeolites; therefore, copper was found to enhance promote desulfurization of oils via converting sulfur compounds into the thermodynamically stable forms between copper and sulfur atoms. Furthermore, Cu-support interaction, and acid strength and pore channel structures of zeolite supports highly affected the sulfur removal from oils. Interestingly, it was revealed that valuable petrochemicals produced by copper-loaded catalysts were benzene, ethylbenzene and cyclohexane for Cu/HY, benzene, toluene and ethylbenzene for Cu/HMOR, and benzene and ethylbenzene for Cu/HBETA. It can indicate that the catalytic pyrolysis of waste tire has high potentials for chemical production as well.

5.2 Introduction

Two facts, known to the tire pyrolysis community, about tire-derived gas and oil are: (1) they contain a considerable amount of sulfur compounds, resulting in strong disturbing odors during uses, and (2) regardless of high aromatic contents, they may contain valuable petrochemicals such as light olefins, cooking gas, mixed-C₄, limonenes, and C₆₋₈ hydrocarbons. Indeed, sulfur in a whole tire (1.4 wt%) can distribute in each part of tire-derived products in different amounts: 10.6 wt% S in gas, 48.8 wt% S in oil, and 40.6 wt% S in carbon black (Kaminsky and Mennerich, 2001). Likely, sulfur in a whole tire (1.5 wt%) distributes in tire-derived products in different amounts: 2.5-5.1 vol% H₂S in gas, while 1.0-1.4 wt% S in oil, and 2.3-2.6 wt% S in char as reported by de Marco Rodriguez *et al.* (2001).

Generally, sulfur species in gas products consist of H₂S, SO₂, COS and CS₂ and H₂S, which are the main sulfur species (Teng *et al.*, 1995; Zhang *et al.*, 2008). Liquid products contain many types of sulfur containing compounds that the main groups were thiophenes, benzothiazoles, benzothiophenes, dibenzothiophenes, and their alkylated derivatives while minor groups were also found such as naphthothiophenes, benzonaphthothiophenes, and their alkylated derivatives (Williams and Besler, 1995; Mastral *et al.*, 2000; Kaminsky and Mennerich, 2001; Unapumnuk *et al.*, 2008). In the main groups of sulfur containing compounds, main species found in the reports as mentioned above were 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 2-ethylthiophene, dibenzothiophene, methyldibenzothiophenes, dimethyldibenzothiophenes and trimethyldibenzothiophenes. In the hydrodesulfurization process, sulfur-polycyclic aromatic hydrocarbons (PASH) can be removed, and the petrochemicals can be produced such as toluene and styrene/ethylbenzene via hydrodesulfurization of 4,6-dimethylbenzothiophene (Dumeignil *et al.*, 2005) and benzothiophene (Yao *et al.*, 2005), respectively. The reports showed the potential of tire-derived oils for petrochemical productions. Since PASH can be desulfurized, resulting in the production of petrochemicals (Dumeignil *et al.*, 2005; Yao *et al.*, 2005) such as toluene, ethylbenzene, styrene, etc.

Copper is an interesting metal because it is a non-noble metal, having a low cost for pyrolysis operation. Furthermore, Cu has potential usable properties beneficial to pyrolysis as well. Cu-loaded catalysts can be used in selective hydrogenation that can remove undesired compounds in the process. For examples, Cu/SiO₂ catalyst was used to remove alkynes and butadiene in C₄-stream by partial hydrogenation reaction converting into butenes (Setiawan and Cavell, 1995). Copper loading on hydrotalcite, malachite, SiO₂ and Al₂O₃ catalysts were used to convert propyne into propylene at high selectivity and undesired products at low selectivity (Bridier *et al.*, 2010). Cu metal was widely used in hydrogenolysis reaction for alcohol production (Chen *et al.*, 2009; Guo *et al.*, 2009). In the other applications, Cu(I)-exchanged zeolites (HY, HY-Al₂O₃, or HBETA) can be used as an adsorbent for thiophene removal from liquid fuels as well (Hernández-Maldonado *et al.*, 2005; Gong *et al.*, 2009; Oliveira *et al.*, 2009; Tang and Shi, 2011). Villarroel *et al.* (2008) used the first row transition metals (Mn, Fe, Co, Ni, Cu and Zn) to promote Mo and W sulfides for sulfur removal of gas-oil containing 2700 ppm in sulfur compounds. They found that at an operating temperature of 325 °C the metal sulfides can generate spillover hydrogen on their surfaces, and then transfer hydrogen atoms to the surface of molybdenum or tungsten sulfides that can enhance hydrodesulfurization activity. Moreover, both quality and quantity of waste tire pyrolysis products can be enhanced by using catalysts. Due to their acid/basic properties and shape selectivity, zeolites were selected to be catalysts for enhancing the products.

For the catalytic pyrolysis of waste tire with the properties mentioned above, copper was expected to promote sulfur removal from oil and increase petrochemical products in oil as well. In this work, the effects of Cu-support interaction on tire-derived oils, petrochemicals and sulfur removal were studied. Cu was impregnated on several zeolites (HBETA, HY and HMOR), and the Cu-support interaction was examined using H₂-TPR. The tire-derived oils were analyzed using a GC×GC-TOF/MS for their chemical composition.

Table 5.1 Calcination conditions of fresh zeolites before using as supports

Zeolite	Calcination Temperature (°C)	Heating Rate (°C/min)	Holding Time at Calcination Temperature (hr)
BETA	600	2	5
Y	500	5	3
MOR	500	5	3

5.3 Methodology

5.3.1 Catalyst Preparation

Three types of zeolites, NH₄-BETA (Si/Al=13.5), HY (Si/Al=7.5), and HMOR (Si/Al=9.5), purchased from TOSOH Company (Singapore) were calcined in static air at the conditions shown in Table 5.1. All calcined zeolites were impregnated with an appropriate amount of a copper solution (Cu(NO₃)₂·3H₂O) to obtain 5 wt% Cu, dried overnight in an oven at 120 °C, and calcined again at the same calcination conditions. Next, the calcined catalysts were reduced at 600 °C for 2 hr in hydrogen atmosphere. Finally, the catalyst powders were pelletized, crushed and sieved to the pellet sizes in the range of 40-60 mesh.

5.3.2 Catalyst Characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuK α radiation operated at 40 kV and 30 mA. The angles in the range of 5 - 65° were scanned at a scanning speed of 5°/min. Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. TPR profiles of catalyst were obtained for comparison of the metal-support interaction of catalysts by using Thermo Finnigan TPDRO 1100 operated at temperature from room temperature to 950 °C with a heating rate of 20 °C/min under 4.99 % H₂/N₂ flow at 20 ml/min. The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min.

Sulfur content on catalyst surface was determined by using LECO®Elemental Analyzer (TruSpec®S).

5.3.3 Waste Tire Pyrolysis

Pyrolysis diagram was the same as in Dũng *et al.* (2009). The catalytic pyrolysis of waste tire was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic zone) with a ramping rate of 10 °C/min and a holding time of 2 hr after the final temperatures were reached. 30 grams of shredded tire (20-40 mesh) and 7.5 grams of a catalyst (40-60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively. Nitrogen gas was used as a carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while the gas products were collected by using a gas sampling bag.

5.3.4 Product Analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solution using a Teflon membrane (0.45 µm) in a vacuum system, and then the maltene solutions were analyzed for the composition by using Gas Chromatography-Mass Spectrometry (GC×GC-TOF/MS). The Agilent gas chromatograph 6890 system consists of a cryogenic modulator and a Pegasus 4D TOF/MS. The 1st column was a non-polar Rtx®-5Sil MS with 30 m × 0.25 mm ID × 0.25 µm film thickness. The 2nd column was an Rxi®-17 MS with 1.10 m × 0.10 mm ID × 0.10 µm film thickness. Furthermore, the true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column (15 m × 0.25 mm × 0.25 µm). The true boiling point curves were 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). The gas products were analyzed for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 µm film thickness and 30 m × 0.32 mm ID).

Furthermore, the liquid and solid products were also analyzed for their sulfur content by using a LECO®Elemental Analyzer (TruSpec®S) whereas the sulfur content in gas products was calculated via mass balance.

5.4 Results and Discussion

5.4.1 Catalyst Characteristics and Cu-Support Interaction

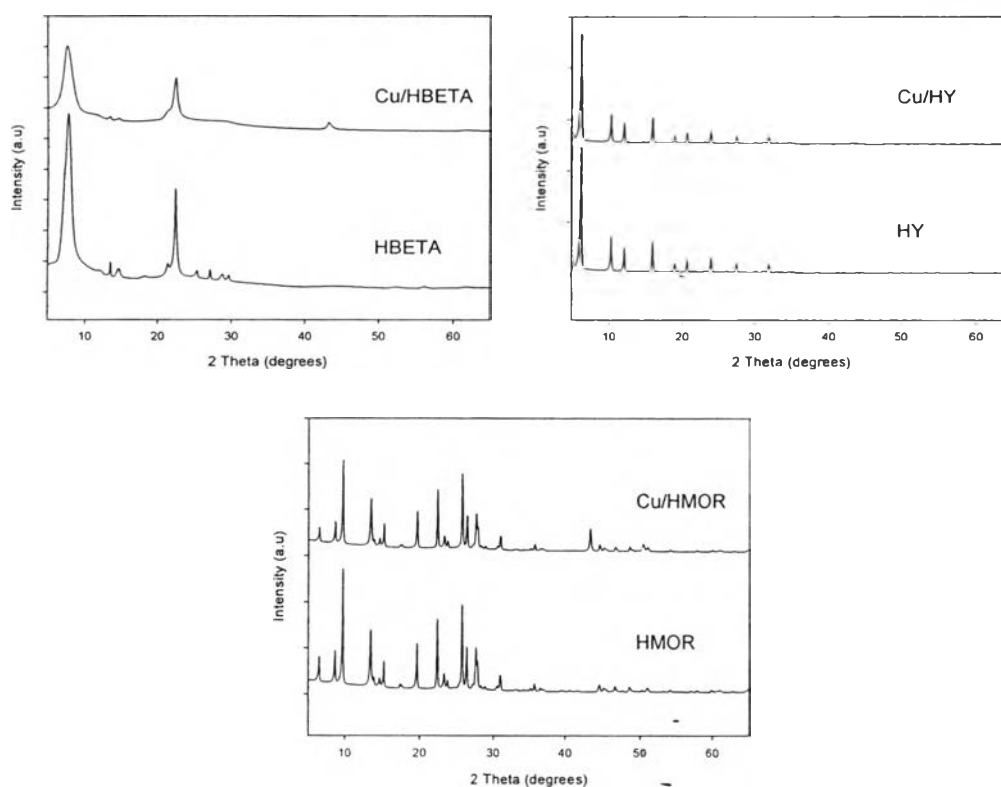


Figure 5.1 XRD patterns of Cu-loaded catalysts.

The XRD patterns of all zeolites and Cu-promoted catalysts are displayed in Figure 5.1. The results show that the introduction of Cu onto all zeolites does not affect zeolite structures. The peaks of Cu appear at the 2θ of 43.47° and 50.67° . Coke deposited on catalyst surface can be acquired from the TG/DTA profiles. The BET specific surface area and pore volume of catalysts are shown in Table 5.2. These results indicate that the introduction of Cu onto all zeolites reduces

the specific surface area and pore volume because copper might partially block the pore of zeolites. The TPR profiles of catalysts are illustrated in Figure 5.2. The profiles can be used to compare the Cu-support interaction of all catalysts. Stronger metal-support interaction is considered from the peak evolving at a higher temperature. The peaks appeared at 477 °C and 377 °C for Cu/HBETA and Cu/HY, respectively, whereas Cu/HMOR gives two reduction peaks at 329 °C and 424 °C. So, it can be concluded that the interaction between Cu-HBETA is stronger than Cu-HMOR and then than Cu-HY.

Table 5.2 BET specific surface area and pore volume of catalysts

Catalyst	BET surface area (m ² /g)	Pore Volume (cm ³ /g)*
HBETA	539	0.257
HY	515	0.266
HMOR	395	0.199
Cu/HBETA	413	0.200
Cu/HY	488	0.256
Cu/HMOR	345	0.180

* Horvath-Kawazoe (H-K) Calculations

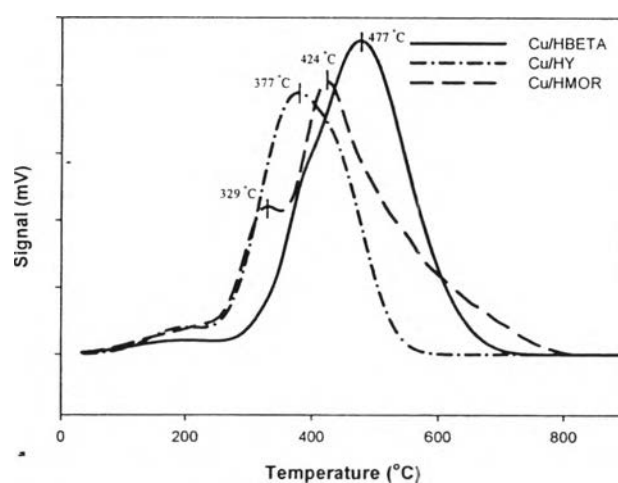


Figure 5.2 TPR profiles of Cu-loaded catalysts.

5.4.2 Tire-derived Oil and Petrochemicals in Oil

Pyrolysis products can be divided into three types based on their phases; that are gas, liquid, and solid. Figure 5.3 shows that the introduction of 5 wt% Cu onto HBETA (Si/Al = 13.5) and HY (Si/Al = 7.5) zeolites increases the gas production, decreases the liquid yields, and increases the amount of coke as well. It indicates that Cu can promote cracking activity of the zeolites. The increment of coke formation can indicate that the activities on the catalyst surface are increased when Cu was loaded. As compared between two zeolites with different Si/Al ratios (HBETA with Si/Al = 13.5 and HY with Si/Al = 7.5). Cu/HY generates slightly higher gas yields than the other catalysts because Cu/HY has higher acid density and higher specific surface area, resulting in higher cracking activity.

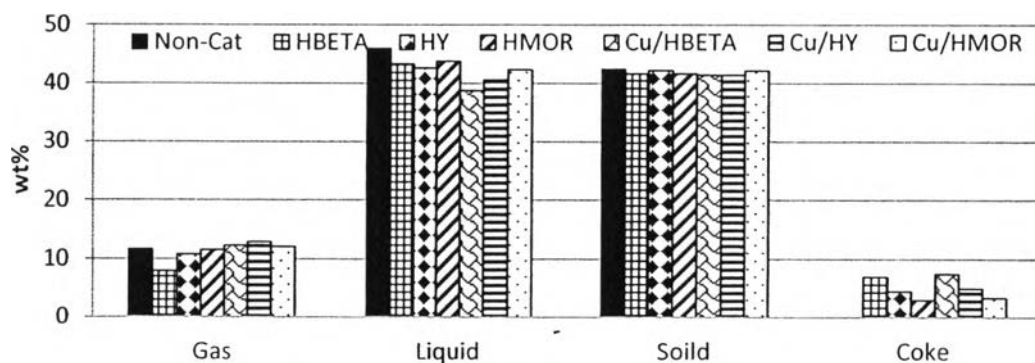


Figure 5.3 Product distribution in the copper-loaded catalyst cases.

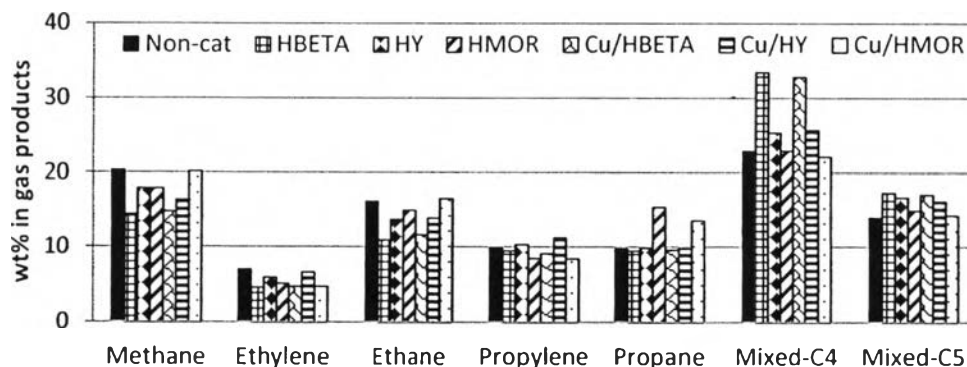


Figure 5.4 Gas compositions in the copper-loaded catalyst cases.

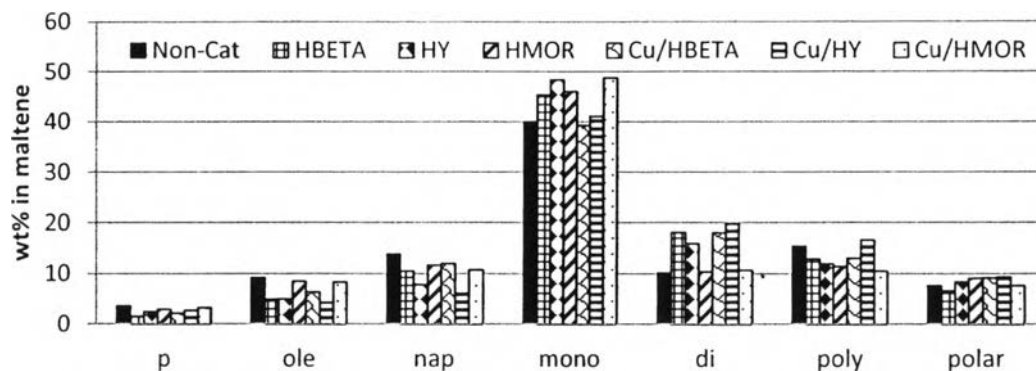


Figure 5.5 Maltene compositions.

In gas analysis as shown in Figure 5.4, the gas compositions are slightly changed, indicating that the presence of Cu on the zeolites does not significantly promote any gas species. Figure 5.5 shows the effect of Cu on the zeolites on maltene compositions. In this work, the components of maltenes are divided into 7 groups; that are, paraffins (p), olefins (o), naphthenes (nap), and mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics (polar). Cu on HBETA and HY decreases the concentration of mono-aromatics. Furthermore, the concentrations of paraffins, olefins and naphthenes are increased in the Cu/HBETA case while the concentrations of di- and poly-aromatics are increased in the Cu/HY case. It can be concluded that Cu/HBETA exhibits hydrogenation and ring-opening activities that convert mono-aromatics into paraffins, olefins and naphthenes, while Cu/HY favors aromatization, producing multi-ring aromatics from mono-aromatics, olefins and naphthenes because HY support has high acid density. The results indicate that small multi-ring aromatic molecules in Cu/HY are also cracked, which is governed by hydrogenation and ring-opening before breaking more C-C bonds (Du *et al.*, 2005) because gasoline is increased in the Cu/HY case as compared with the HY case. So, Cu on both zeolites also promotes hydrogenation and ring-opening activities. The higher acid density and specific surface area of Cu/HY (higher cracking activity) also cause the lighter hydrocarbon molecules in maltene than Cu/HBETA.

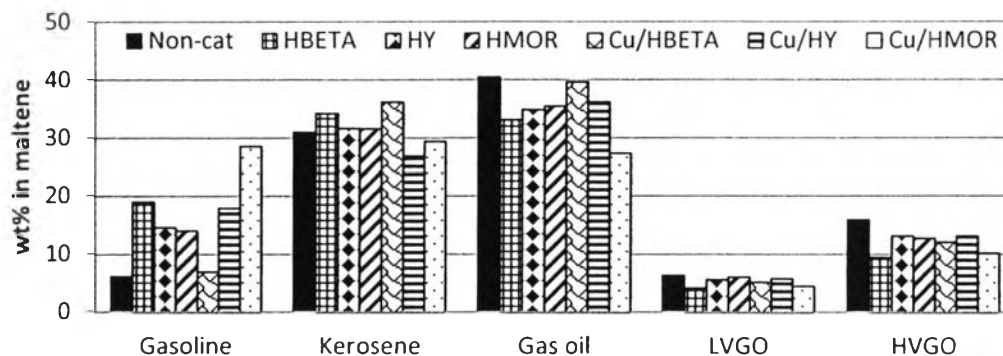


Figure 5.6 Petroleum cuts of maltene in Cu-loaded catalysts.

Copper on HMOR can increase the concentration of mono-aromatics in maltene via hydrogenation and ring-opening of poly-aromatics, and via aromatization of naphthenes. Furthermore, gasoline is also highly increased because copper promotes cracking activities. As compared between Cu on two zeolites with different pore channel structures (HY with 3 Dimensional pore channel structure and HMOR with 1 Dimensional pore structure), Cu/HMOR produces higher single ring-aromatics content in maltene than Cu/HY because 1D pore channel structure might be proper to mono-aromatic production from cracking poly-aromatics, while Cu/HY with 3D pore structure favors the productions of multi-ring aromatics because 3D pore channel structure catalyst has too much open space (pore size and architecture) for aromatization, resulting in lower concentration of olefins and higher bulky aromatics in oils (Bortnovsky *et al.*, 2005). However, the higher surface area of Cu/HY causes the higher cracking activity (higher gas yield) and the greater sulfur removal from the oil.

Copper addition can increase gasoline fraction in oils, except Cu on HBETA since Cu/HBETA highly cracks hydrocarbons in the gasoline range to smaller molecules in the gas phase more than the other Cu-loaded catalysts. It can be explained that the strong Cu-HBETA interaction results in low sulfur deposition on the Cu surface that is the active sites for hydrogenation, cracking, and ring-opening. Moreover, the GC×GC-TOF/MS results indicate that the main compositions of oil are aromatics in all petroleum cuts (Table 5.3). So, tire-derived oils are not quite suitable for being used directly as fuels.

Table 5.3 Composition of each petroleum cuts

	Gasoline	Kerosene	Gas Oil	LVGO	HVGO
Paraffins	0.00-1.92	0.806-1.69	3.95-11.6	0.00-13.5	0.00-23.9
Olefins	2.69-11.3	4.55-9.04	4.46-9.51	0.00-22.3	-
Naphthenes	7.85-13.8	4.77-13.0	5.12-16.8	0.00-22.0	-
Aromatics	75.5-84.7*	76.3-90.0	65.4-81.1	71.1-100	76.1-100

* 37.5 – 71.9 wt% of mono-aromatics in gasoline

In tire-derived oil, petrochemicals can be formed two ways: (1) conversion of hydrocarbons, and (2) conversion of sulfur-containing compounds.

The petrochemicals productivity and selectivity in gasoline (Table 5.4 and Figure 5.7) are increased when Cu was loaded on HY and HMOR zeolite. With the same reason, Cu on HBETA highly promotes cracking reaction of small molecules (including these petrochemicals) in the gasoline range, forming gases; so, the selectivity of petrochemicals in the Cu/HBETA case is the lowest among those of all catalytic cases.

Table 5.4 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
Cu/HBETA	4.74
Cu/HY	52.3
Cu/HMOR	43.0

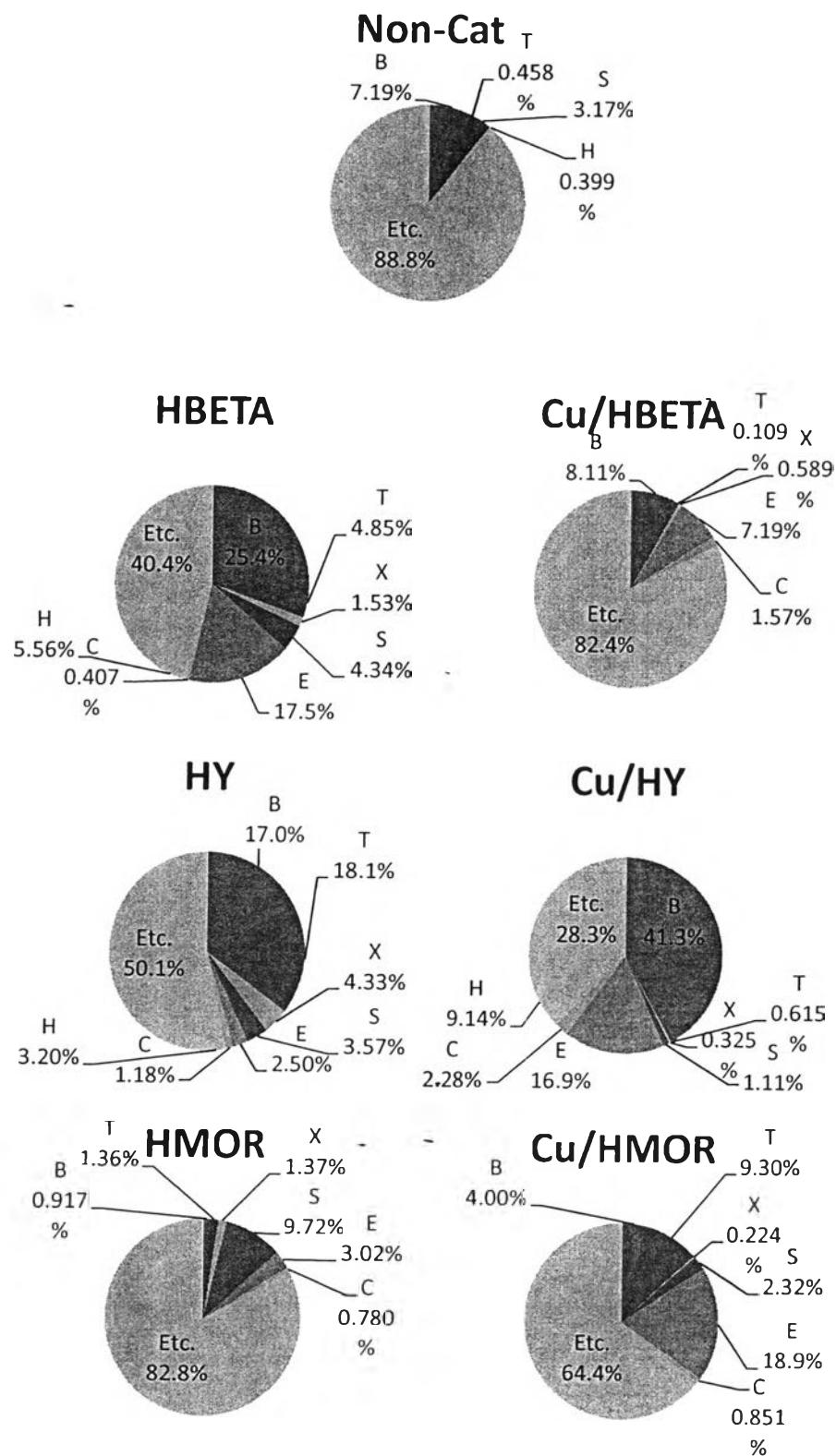


Figure 5.7 Selectivity of petrochemicals in gasoline range products.

An example of desulfurization of sulfur-containing compounds that results in the formation of petrochemicals is shown in Figures 5.8-5.10. Cu on HY and HMOR reduces the amount of total BTz and ITC yields as compared with pure HY and HMOR cases, indicating that BTz and ITC can be converted into benzene. Furthermore, Cu/HY catalyst promotes benzene, ethylbenzene and cyclohexane production because Cu/HY might promote hydrogenation and dealkylation of HY. Cu/HMOR catalyst highly produces ethylbenzene, toluene and benzene because Cu/HMOR might increase dealkylation activity.

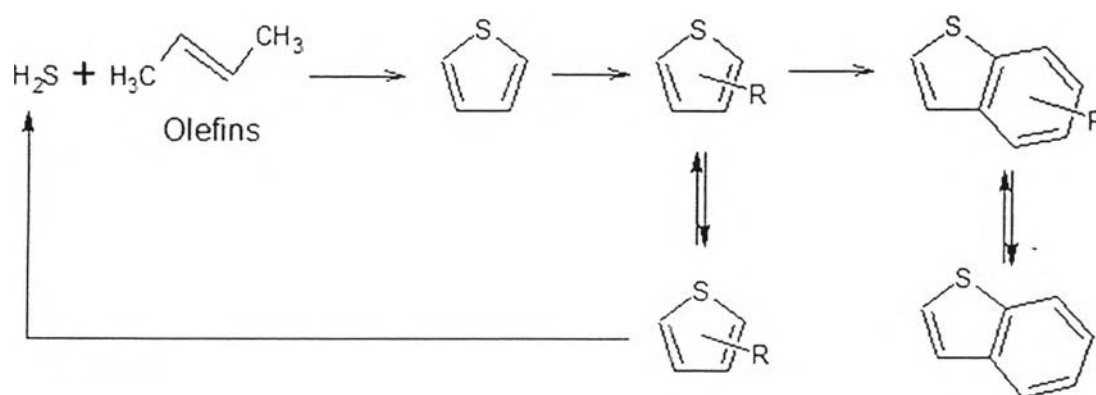


Figure 5.8 An example of sulfur-containing compounds formation via a reaction of hydrogen sulfide and olefins (Corma *et al.*, 2001).

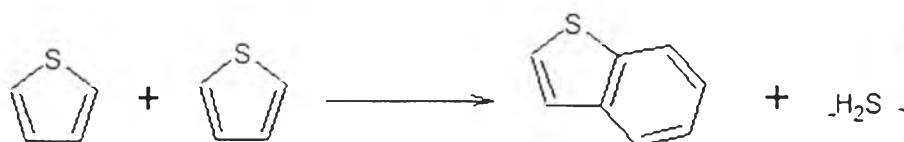


Figure 5.9 Benzothiophene production from thiophene (Yu *et al.*, 1999).

Even though the amount of sulfur-containing compounds is markedly lower than that of petrochemicals and/or gasoline, the increase of petrochemical production is highly increased because Cu-support interaction might strongly affect the petrochemical production. Cu-support interaction can relate to the adsorption of sulfur-containing compounds and desorption of sulfur atoms on the catalyst surface

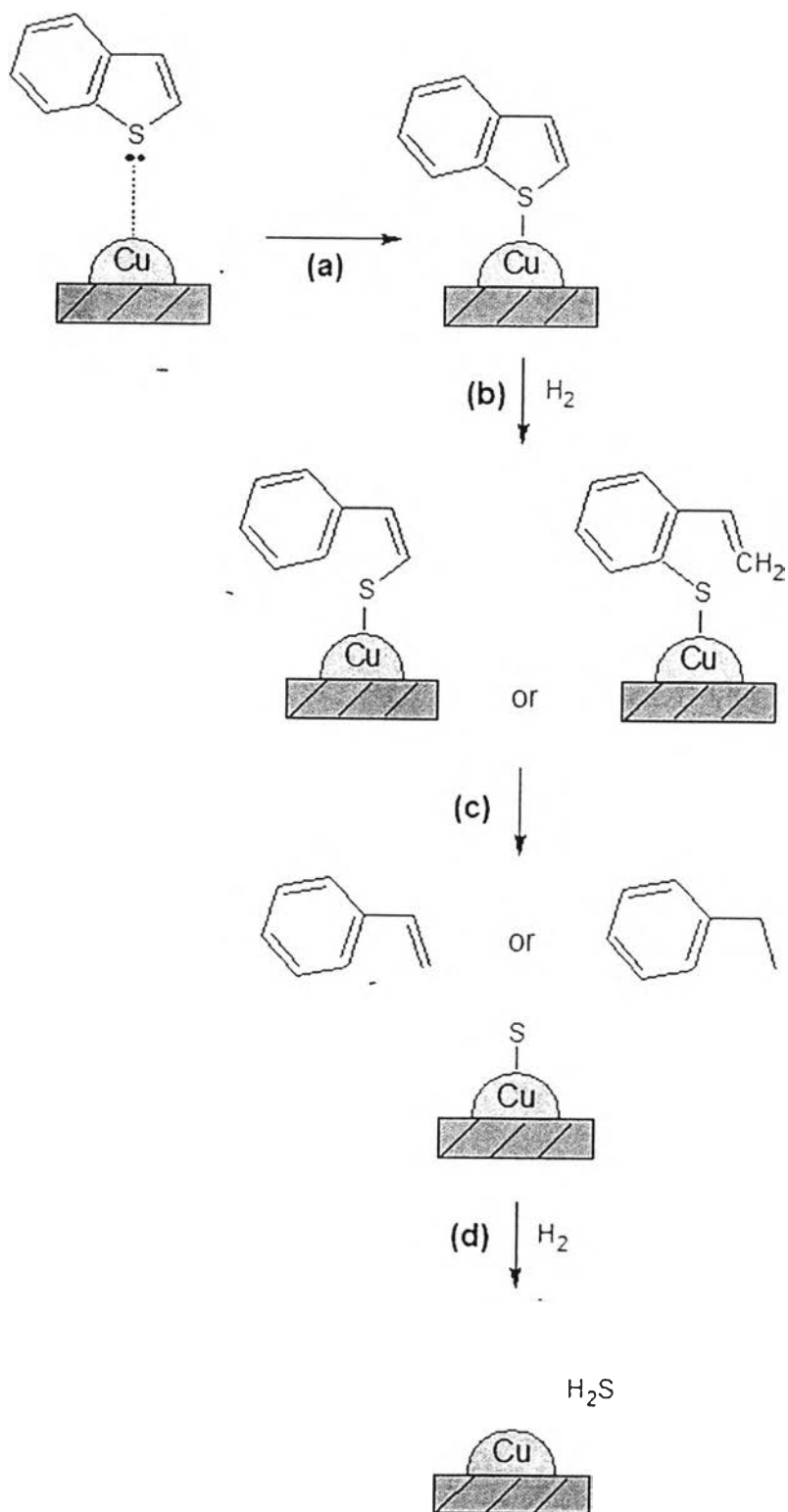


Figure 5.10 Sulfur removal pathway of benzothiophene.

via reacting with hydrogen to form H₂S and/or hydrocarbons to form thiophenes. The desorption of sulfur atoms on the catalyst surface can form the molecular structures, similar to the sulfur-containing compounds that can also re-adsorb and form petrochemicals. Figures 5.8 and 5.9 (Yu *et al.*, 1999; Corma *et al.*, 2001) show the formation of benzothiophenes from H₂S and olefins or from thiophenes. The example of pathways to produce petrochemicals from sulfur-containing compounds is shown in Figure 5.10.

5.4.3 Sulfur Compounds in Oil and Sulfur Removal

Metal-Support Interaction:

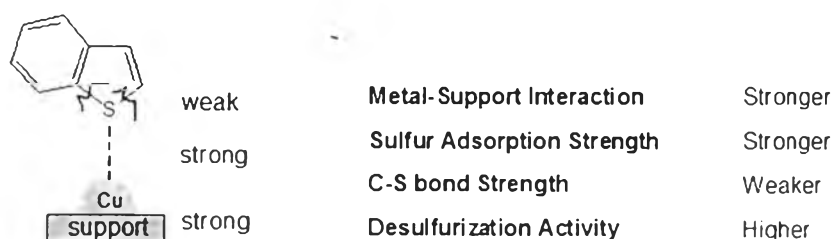


Figure 5.11 Effect of metal-support interaction on desulfurization activity.

Desulfurization can be divided into four steps; (a) the adsorption of an S-compound on a Cu-site, (b) the hydrogenation of the adsorbed S-compound and C-S bond breaking, (c) the desorption of a hydrocarbon and copper sulfide formation, and (d) the removal of S atoms on the surface (surface cleaning) as seen in Figure 5.10. Each step can be related to the Cu-support interaction. The TPR profiles of catalysts are plotted in comparison in Figure 5.2. Stronger metal-support interaction is considered from the peak evolving at a higher temperature. From the profiles, it can be concluded that the metal-support interaction between Cu-HY is weaker than Cu-HMOR and then Cu-HBETA. Strong Cu-HBETA interaction (High electron deficiency) causes high S-compound adsorption strength, which makes the adsorbate so unstable that the C-S bond can be easily broken, and then sulfur can be removed easily. Therefore, in this situation, the release of an S-free hydrocarbon molecule from the Cu/HBETA surface can occur easily, resulting in the lowest sulfur content in oils as compared with other Cu-loaded catalysts in Table 5.5. On the other hand,

Cu/HY and Cu/HMOR that have weaker metal-support interaction than Cu/HBETA, so they can adsorb an S-compound with lower strength, and a hydrocarbon cannot be easily released. For surface cleaning, Cu/HBETA with the stronger metal-support interaction might have the lowest number of electrons in the highest occupied molecular orbitals (HOMO) of Cu, occupying antibonding orbitals, among the other Cu-loaded catalysts, resulting in the highest Cu-S bond strength in copper sulfide. Thus, it is the most difficult to remove sulfur atoms on the spent Cu/HBETA surface among those of the other spent catalysts (Chianelli *et al.*, 2002). This is supported by a high distribution of S on the spent Cu/HBETA catalyst as illustrated in Figure 5.12. Therefore, Cu/HBETA seems to be the best catalyst in terms of the activity on sulfur removal from the tire-derived oils.

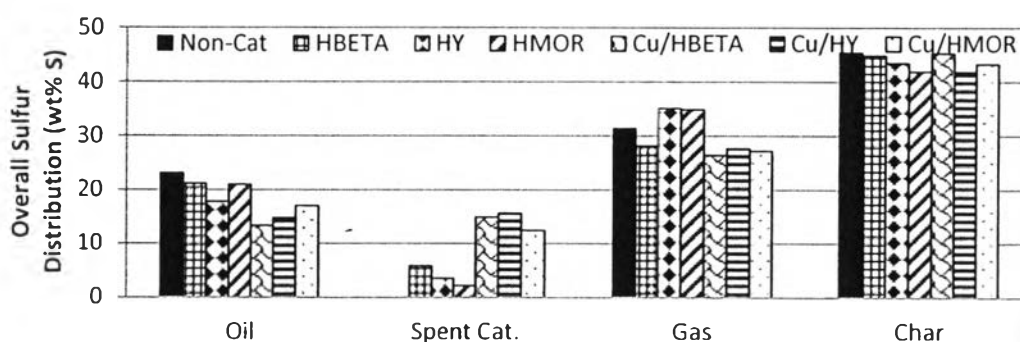


Figure 5.12 Overall sulfur distribution of Cu-loaded catalysts.

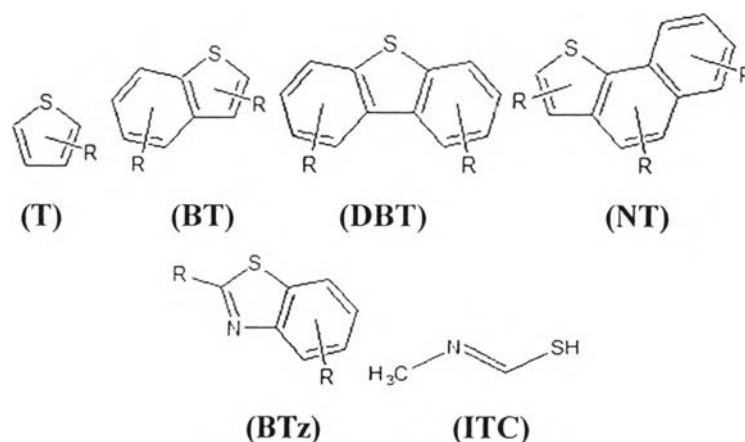


Figure 5.13 Major sulfur-containing compounds in tire-derived oils.

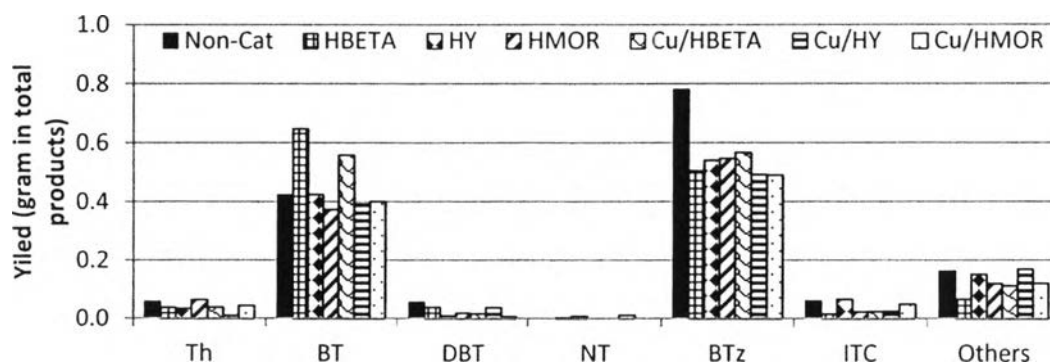


Figure 5.14 Sulfur-containing species in maltenes.

Table 5.5 Sulfur content in oil (wt%)

Catalyst	wt% Sulfur in oil
No Catalyst	1.14
HBETA	1.10
HY	0.943
HMOR	1.08
Cu/HBETA	0.778
Cu/HY	0.820
Cu/HMOR	0.907

Sulfur-containing compounds can be classified into six groups: thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC) as shown in Figure 5.13. Total Th, BT and DBT yields are decreased in all copper-loaded catalyst cases (Figure 5.14) because copper can react with sulfur atoms in the compounds, and can form the thermodynamically stable form such as CuS or Cu₂S. It can be indicated that copper can promote sulfur removal activity.

5.5 Conclusions

Copper can be used to promote sulfur reduction from tire-derived oils of zeolites because it has sulfur adsorption properties. Sulfur content in oil of the copper-loaded catalysts was 0.778 wt%, 0.82 wt%, and 0.907 wt% in oil for Cu/HBETA, Cu/HY, and Cu/HMOR cases, respectively. The important effects of catalysts on sulfur removal are zeolite properties and Cu-support interaction. The catalysts with strong Cu-support interaction have high ability to adsorb sulfur on their surfaces. The removal of sulfur from sulfur-compounds can also result in the production of petrochemicals because the main species of sulfur-containing compounds have the molecular structures similar to several types of petrochemicals. Furthermore, the tire-derived oils are a potential alternative source for petrochemical production because the oils were composed of the high amount of aromatics, especially mono-aromatics. Interestingly, the introduction of copper highly promoted the production of valuable products in oils as well. The results indicated that copper on HY and HMOR zeolites had ability on enhancing the petrochemical productivity. Cu/HY highly produced benzene, ethylbenzene and cyclohexane, Cu/HMOR highly produced benzene, toluene and ethylbenzene, while Cu/HBETA did not promote petrochemical production as compared with HBETA.

5.6 Acknowledgements

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5.7 References

Bortnovsky, O., Sazama, P., and Wichterlova, B. (2005) Cracking of pentenes to C2–C4 light olefins over zeolites and zeotypes: Role of topology and acid site strength and concentration. *Applied Catalysis A: General*, 287, 203-213.

- Bridier, B., López, N., and Pérez-Ramírez, J. (2010) Partial hydrogenation of propyne over copper-based catalysts and comparison with nickel-based analogues. Journal of Catalysis, 269, 80-92.
- Chen, L.-F., Guo, P.-J., Zhu, L.-J., Qiao, M.-H., Shen, W., Xu, H.-L., and Fan, K.-N. (2009) Preparation of Cu/SBA-15 catalysts by different methods for the hydrogenolysis of dimethyl maleate to 1,4-butanediol. Applied Catalysis A: General, 356, 129-136.
- Chianelli, R.R., Berhault, G., Raybaud, P., Kasztelan, S., Hafner, J., and Toulhoat, H. (2002) Periodic trends in hydrodesulfurization: in support of the Sabatier principle. Applied Catalysis A: General, 227(1-2), 83-96.
- Corma, A., Martínez, C., Ketley, G., and Blair, G. (2001) On the mechanism of sulfur removal during catalytic cracking. Applied Catalysis A: General, 208(1-2), 135-152.
- de Marco Rodriguez, I., Laresgoiti, M.F., Cabrero, M.A.; Torres, A., Chomón, M.J., and Caballero, B. (2001) Pyrolysis of scrap tyres. Fuel Processing Technology, 72, 9-22.
- Du, H., Fairbridge, C., Yang, H., and Ring, Z. (2005) The chemistry of selective ring-opening catalysts. Applied Catalysis A: General, 294(1), 1-21.
- Dumeignil, F., Sato, K., Imamura, M., Matsubayashi, N., Payen, E., and Shimada, H. (2005) Characterization and hydrodesulfurization activity of CoMo catalysts supported on sol-gel prepared Al₂O₃. Applied Catalysis A: General, 287(1), 135-145.
- Dũng, N.A., Wongkasemjit, S., and Jitkarnka, S. (2009) Effects of pyrolysis temperature and Pt-loaded catalysts on polar-aromatic content in tire-derived oil. Applied Catalysis B: Environmental, 91, 300-307.
- Gong, Y., Dou, T., Kang, S., Li, Q., and Hu, Y. (2009) Deep desulfurization of gasoline using ion-exchange zeolites: Cu(I)- and Ag(I)-beta. Fuel Processing Technology, 90, 122-129.
- Guo, L., Zhou, J., Mao, J., Guo, X., and Zhang, S. (2009) Supported Cu catalysts for the selective hydrogenolysis of glycerol to propanediols. Applied Catalysis A: General, 367(1-2), 93-98.

- Hernández-Maldonado, A.J., Yang, F.H., Qi, G., and Yang, R.T. (2005) Desulfurization of transportation fuels by π -complexation sorbents: Cu(I)-, Ni(II)-, and Zn(II)-zeolites. Applied Catalysis B: Environmental, 56, 111-126.
- Kaminsky, W. and Mennerich, C. (2001) Pyrolysis of synthetic tire rubber in a fluidised-bed reactor to yield 1,3-butadiene, styrene and carbon black. Journal of Analytical and Applied Pyrolysis, 58-59, 803-811.
- Mastral, A.M., Murillo, R., Callen, M.S., Garcia, T., and Snape, C.E. (2000) Influence of process variables on oils from tire pyrolysis and hydrolysis in a swept fixed bed reactor. American Chemical Society, 14, 739-744.
- Oliveira, M.L.M., Miranda, A.A.L., Barbosa, C.M.B.M., Cavalcante Jr, C.L., Azevedo, D.C.S., and Rodriguez-Castellon, E. (2009) Adsorption of thiophene and toluene on NaY zeolites exchanged with Ag(I), Ni(II) and Zn(II). Fuel, 88, 1885-1892.
- Setiawan, I. and Cavell, K.J. (1995) Removal of unsaturated contaminants from an industrial C4-stream using Cu/SiO₂ catalysts: Subsequent testing of the purified stream with an alkyne sensitive catalyst system. Applied Catalysis A: General, 131, 225-241.
- Tang, X.-L. and Shi, L. (2011) Study of the adsorption reactions of thiophene on Cu(I)/HY-Al₂O₃ by Fourier transform infrared and temperature-programmed desorption: Adsorption, desorption, and sorbent regeneration mechanism. Langmuir, 27, 11999-12007.
- Teng, H., Serio, M.A., Whjtowicz, M.A., Bassilakis, R., and Solomon, P.R. (1995) Reprocessing of used tires into activated carbon and other products. Industrial and Engineering Chemistry Research, 34, 3102-3111.
- Unapumnuk, K., Keener, T.C., Lu, M., and Liang, F. (2008) Investigation into the removal of sulfur from tire derived fuel by pyrolysis. Fuel, 87, 951-956.
- Villarroel, M., Baeza, P., Escalona, N., Ojeda, J., Delmon, B., and Gil-Llambías, F.J. (2008) M_D/Mo and M_D/W [M_D = Mn, Fe, Co, Ni, Cu and Zn] promotion via spillover hydrogen in hydrodesulfurization. Applied Catalysis A: General, 345, 152-157.

- Williams, P.T. and Besler, S. (1995) Pyrolysis-thermogravimetric analysis of tyres and tyre components. Fuel, 74, 1277-1283.
- Yao, X.-Q., Li, Y.-W., and Jiao, H. (2005) Mechanistic aspects of catalyzed benzothiophene hydrodesulfurization. A density functional theory study. Journal of Molecular Structure: THEOCHEM, 726(1-3), 67-80.
- Yu, S.Y., Li, W., and Iglesia, E. (1999) Desulfurization of Thiophene via Hydrogen Transfer from Alkanes on Cation-Modified H-ZSM5. Journal of Catalysis, 187, 257-261.
- Zhang, X., Wang, T., Ma, L., and Chang, J. (2008) Vacuum pyrolysis of waste tires with basic additives. Waste Management, 28(11), 2301-2310.