PLATINUM LOADED ON FIBROUS ZSM-5 FOR CUMENE HYDROCRACKING

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PLATINUM LOADED ON FIBROUS ZSM-5 FOR CUMENE HYDROCRACKING

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Specially dedicated to my amazing father and mother

Drajat Sudrajat and Rustiah

&

My beloved ones

“Thank you for the endless support and everything “

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ABSTRACT

Recently, the need to create a versatile hydrocracking catalyst is a major concern in oil and gas industry. The increasing demand for valuable middle distillates has placed hydrocracking as the most important secondary process. Cumene hydrocracking is an ideal hydrocracking reaction due to the minimum amount of side reactions. A novel ZSM-5 catalyst with fibrous morphology (FZSM-5) and platinum loaded on FZSM-5 (Pt/FZSM-5) were successfully prepared by using a microemulsion system with ZSM-5 seed assisted crystallization and impregnation method for cumene hydrocracking. XRD and FESEM/TEM-EDX analyses showed that the FZSM-5 possesses ZSM-5 structure and a spherical morphology with evenly distributed dendrimeric silica fibers. In addition, FZSM-5 exhibited intrinsic mesopores at 3-5 and 10-20 nm, which led to an increase in the surface area up to 42% compared with ZSM-5 seed. Pyridine FTIR result showed the presence of a large number of Lewis acid sites and a small number of Brönsted acid sites. These acid sites were further increased after protonation and introduction of platinum. In addition, the protonation and introduction of Pt on FZSM-5 increased the rate of cumene conversion up to 0.303 μmole/s g-cat at 623 K with 92% product yield in which the product equally distribute to benzene and propylene. This activity of Pt/HFZSM-5 in cumene hydrocracking was almost 1.5-fold higher than that of Pt/HZSM-5 (0.161 μmole/s g-cat) with 72% product yield. The high activity of Pt/HFZSM-5 towards cumene hydrocracking could be attributed to the unique morphology of FZSM-5 which increase the accessibility of the active sites and facilitated the hydrogen spillover phenomena assisted by the presence of a large number of Lewis acid sites and platinum metal. This new fibrous ZSM-5 catalyst open a big potential in general heterogeneous catalytic reaction, especially in the hydrocracking process.

ABSTRAK

Baru – baru ini, keperluan untuk mewujudkan mangkin pemecahan hidro yang serba boleh telah menjadi tumpuan utama dalam industri minyak dan gas. Peningkatan terhadap permintaan hasil sulingan peringkat pertengahan yang bernilai telah meletakkan pemecahan hidro sebagai proses sekunder yang paling penting. Pemecahan hidro kumena adalah tindak balas pemecahan hidro yang ideal kerana menghasilkan tindak balas sampingan yang minimum. Mangkin ZSM-5 yang mempunyai morfologi berserat (FZSM-5) dan mangkin FZSM-5 termuat platinum (Pt /HFZSM-5), telah berjaya disediakan melalui sistem mikroemulsi dengan penghabluran berbantukan benih ZSM-5 dan kaedah pengisitepuan untuk pemecahan hidro kumena. Analisis XRD dan FESEM / TEM-EDX menunjukan bahawa FZSM-5 mempunyai struktur ZSM-5 dan morfologi sfera dengan serat silika berdendrimer tertabur sekata. Tambahan itu, FZSM-5 juga menunjukkan liang meso yang intrinsik pada 3-5 dan 10-20 nm, yang meningkatkan luas permukaan sehingga 42% berbanding dengan benih ZSM-5. FTIR piridina pula menunjukkan kewujudan sejumlah besar tapak asid Lewis dan sebilangan kecil pula tapak asid Brönsted. Tambahan lagi, pemprotonan dan pengenalan Pt pada FZSM-5 juga meningkatkan kadar penukaran kumena sehingga 0.303 μmole/s g-cat pada 623 K dengan 92% hasil produk dimana hasil benzena dan propilena adalah sama banyak. Aktiviti Pt / HFZSM-5 dalam pemecahan hidro kumena adalah hampir 1.5 kali ganda lebih tinggi daripada Pt / HZSM-5 (0.161 μmole/s g-cat) dengan hasil produk 72%. Aktiviti tinggi mangkin Pt / HFZSM-5 terhadap pemecahan hidro kumena boleh dikaitkan dengan morfologi unik FZSM-5 yang memudahkan capaian tapak aktif dan membantu fenomena limpahan hidrogen berbantukan kehadiran sebilangan besar tapak asid Lewis dan logam platinum. Mangkin ZSM-5 baharu ini dengan morfologi berserat mempunyai potensi besar dalam mempelopori tindak balas pemangkinan heterogen, terutama dalam proses pemecahan hidro.

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LIST OF SYMBOLS

Å - Angstrom

K - Kelvin

kV - Kilovolt

μmole - Micromole

mA - Miliampere

mL - Mililiter

min - Minutes

M - Molar

nm - nanometer

% - Percentage

θ - Theta

W - Watt

wt % - Weight Percentage

LIST OF ABBREVIATIONS

BET	-	Braunauer-Emmett-Teller
BJH	-	Barret-Joyner-Halenda
EDX	-	Electron Dispersive X-ray
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
HFZSM-5	-	Protonated Fibrous ZSM-5
HZSM-5	-	Protonated ZSM-5
KCC-1	-	KAUST Catalysis Center – 1
MFI	-	Mordenite Framework Inverted
MAS NMR	-	Magic Angle Spinning Nuclear Magnetic Resonance
Pt	-	Platinum
Pt/HFZSM-5	-	Platinum Loaded HFZSM-5
Pt/HZSM-5	-	Platinum Loaded HZSM-5
Si	-	Silica
TEM	-	Transmission Electron Microscope
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Energy has big influence in human daily life and social activity. This has placed energy at the vital point in the development of modern human society. Modern societies consume massive energy that comes from the combustion of fossil fuels. The world population still grows at an exponential rate. According to a report by United Nation in 2004, the world population will reach 8.9 billion in 2040 and further escalate to 11 billion in 2050. Along with the population growth, the demand for energy will also increase. Nowadays, oil has been dominated as the main energy source and this position will probably continue in the next decade due to the maturity of the process technology (Primo and Garcia, 2014).

Global concern regarding the environment and health led to more complex system of refinery (Weyda and Kohler, 2003). This is the consequence of several legislative actions taken by several nations. After the invention of unleaded-gasoline in early 1970, minimizing the sulfur, aromatic content, and also the prohibition of methyltertiarybutylether (MTBE) as a gasoline additive have summed up the environmental issues that have reformed the refining industry. The reforming of light naphtha and heavy oil is the favorable processes to overcome this problem (Kubo, *et al.*, 2012). The refinery and petrochemistry efficiency depends solely on catalyst activity, selectivity and durability (Marcilly, 2000; Degnan, 2003). Production of heavy crude oil world-wide is increasing year-by-year (Acheyta, *et al.*, 2005). According to U.S Energy Information Administration (EIA), oil consumption increases up to 9.6 million barrels per day from 2012 to 2019 and reaches its peak in 2021.

According to U.S EIA report, the production of light oil has been declining while heavy oil production has increased significantly. At this time, machinery and equipment are designed to run using liquid fuel, resulting in the need to upgrade heavy oil into much useful product. Heavy oil has high viscosity which makes them difficult to transport via pipeline because their inability to flow freely and require high energy to overcome the pressure loss in the pipeline. Heavy oil also contains high levels of contaminants such as sulfur, metal, sphaltenes, carbon residue, and solid particle which made the direct application is impractical (Hart, 2013). These problems have placed the conversion of heavy oil fraction into valuable liquid products such as gasoline, diesel, and jet fuel to be one of the most important processes in upgrading heavy oil (Yang, *et al.*, 1998)

The conversion of heavy oil fraction can be achieved by thermal, catalytic, and hydrocracking (Yang, *et al.*, 1998). Thermal cracking is not favorable due to production of lower quality of gas and naphtha. While for catalytic cracking, rapid build up of coke and production of olefin/aromatic in significant amount are inevitable. These occur due to the absence of hydrogen partial pressure. Hydrocracking is the most versatile and favorable process in petrol refinery due to its feasibility. There is flexibility in feedstock and product which is the advantage, hence provides the balanced in supply and demand in economical point of view. There are wide varieties of commercial feedstocks ranging from light naphtha to heavy crude oil and numerous choices of catalysts make it possible to produce high octane gasoline and other middle distillate at one time (Choudary and Saraf., 1975).

Hydrocracking requires a bifunctional catalyst that able to promote hydrogenation of the hydrocarbon and provide acidity. Conventional catalyst for hydrocracking contains metal that provides the hydrogenation ability. Metal such as nickel, molybdenum, iron, tungsten, platinum, ruthenium, palladium, cobalt, and chromium have been reported to increase the activity of catalysts (Annuar, *et al.*, 2014; Li, *et al.*, 2015; Han, *et al.*, 2014; Serrano, *et al.*, 2015; Pudukudy, *et al.*, 2015). Hydrocracking catalyst requires a solid support with acidic function where several supports have been reported such as, γ-Al_2O_3, SiO_2, ZrO_2, silica nanoparticle, and zeolites (Annuar, *et al.*, 2014; Sazegar, *et al.*, 2014; Kubo, *et al.*, 2012; Kweon, *et al.*, 2014). In order to achieve good performance in hydrocracking, the catalyst requires a good balance between these two functions (Campbell and Wojciechowski, 1971). Cumene hydrocracking has been used as a good measure for hydrocracking catalyst. This is due to the simplicity of the reactions. Cumene hydrocracking does not complicate with a significant amount of side reactions, such as isomerization and/or chain lengthening. Currently, the catalysts for cumene hydrocracking are facing problems such as rapid deactivation, unstable structure, high temperature reaction and low selectivity of desired product and conversion of reactant.

Zeolite possesses catalytically active site and uniformity in micropore size and shape in which make zeolite as a suitable catalyst in the oil refining. However, due to the constraints in pore diameter, zeolite catalytic activity significantly decreased when facing a bulky molecule with a kinetic diameter above 7 Å (Maesen, *et al.*, 2004). Microporous zeolite such as Y, ZSM-5, and β plays an important role in petrochemical industry due to their microporous structure and strong intrinsic acidity. The development of mesopore in microporous zeolite has been proved to solve the diffusion limitation and pore blockage that conventional zeolite faced (Meng, *et al.*, 2009). However, the catalytic activity of the catalyst can still be enhanced by increasing the accessibility of the active site and better metal dispersion.

Fibrous material was initially developed by Polshettiwar, *et al.* in 2010. The first fibrous material is a silica-based equipped with high surface area and better accessibility of active site. Several studies showed the potential of silica-based fibrous material in the adsorption of nitro- and chloro- compounds and hydrogenolysis of alkene (Fihri, *et al.*, 2014). Silica-based fibrous material was developed by using microemulsion technique which originally comes from surfactant. Although utilization of surfactant in zeolite synthesis has been explored in many years, up to this time of study, the development of zeolite-based fibrous material has never been reported. Development of zeolite-based fibrous material will significantly improve their catalytic activity, along with tunable acidity, high surface area, and better accessible active site. Zeolite-based fibrous material will have a great potential to be applied in oil and gas industry.

1.2 Problem Statement and Hypothesis

The increase in production of crude oil and demand for light and middle distillates, such as gasoline, diesel, and kerosene, has placed hydrocracking into important secondary process in oil refinery. However, hydrocracking requires an efficient bifunctional catalyst to achieve the highest conversion of heavy oil. Since hydrocracking requires an acidic solid support, there are wide varieties of support that have adequate amount of acid sites. γ-Al_2O_3 has been widely used in hydrocracking due to its mild acidity. However, γ-Al_2O_3 requires high temperature to obtain the high conversion in hydrocracking. Other than that, SiO_2 which has high surface area also been used as acidic support in hydrocracking. However, SiO_2 only has weak Brönsted acid in their surface and therefore hardly developed catalytic activity. In contrary, ZrO_2 presents a high surface area, but requires modification with tungstate or sulfate to increase their thermal stability and surface acidity (Reddy and Reddy, 2000).

Zeolites such as Y, ZSM-5, and β have been employed as a catalyst in the hydrocracking process due to their tunable intrinsic acidity, surface area, and uniform pores. Zeolite consists of silica-alumina framework provides with good thermal stability and wide varieties of Si/Al ration provide with good tunable acidity. Zeolite is a suitable material for facilitating acid-catalyzed reactions. However, their drawbacks such as diffusion and accessibility of active site limitations have been constrained the zeolite catalytic activity. Great efforts have been conducted to overcome the diffusion limitation, where development of hierarchically porous zeolite is one of the most versatile pathways. This material has proven to increase the catalyst ability in isomerization, alkylation, and cracking (Teh, *et al.*, 2015).

Ordered mesoporous material is one of the most interesting discoveries in the field of material synthesis. Mesoporous material such as MCM-41, MCM-48, and SBA-15 has been used as cracking catalyst. Mesoporous material possesses highly ordered mesoporous structures which enabled the size-selectivity and extremely high surface area with large pore volume (Zhao, *et al.*, 2012). However, mesoporous material has lower acidity and thermal stability compared with amorphous Si-Al and zeolite Y resulting in lower catalytic activity (Corma, 1997).

Silica-based fibrous material has the advantage of high surface area due to the presence of the dendrimeric fiber. Silica-based fibrous material also has better accessibility of active site because the dispersion of active sites probably located in their dendrimeric fiber rather than inside the catalyst pore. Silica-based fibrous material also possesses high thermal stability (Polshettiwar,, *et al.*, 2010). Because the fibrous material is fully composed with silica, it doesn’t have adequate acid sites to promote acid-catalyzed reaction such as isomerization process.

Implementation of the concept in developing silica-based fibrous material to zeolite will be the key to overcome these problems. Zeolite with dendrimeric silica fiber will have better access to active sites. This is because, instead of inside the pore, the active sites will be accessible at the dedrimeric area. This will lead to low diffusion limitation, because the reactant does not need to diffuse into zeolite pores. Because the presence of the dendrimeric fiber, the surface area will also increase and it will increase the dispersion of metal active sites. Utilizing microemulsions method the development of zeolite-based fibrous material will be successfully achieved. Zeolite-based fibrous material is the next step towards an efficient heterogeneous catalyst for hydrocracking.

1.3 Objectives

The objectives of this study are:

1. To prepare fibrous ZSM-5 (FZSM-5), protonated FZSM-5 (HFZSM-5), and platinum loaded on HFZSM-5 (Pt/HFZSM-5) catalysts.
2. To characterize the physical and chemical properties of FZSM-5, HFZSM-5, Pt/HFZSM-5 and Pt/HZSM-5 catalysts.
3. To study the psychochemical relationship of Pt/HZSM-5, HFZSM-5, and Pt/HFZSM-5 catalysts in cumene hydrocracking.
4. To study the performance and stability of the catalyst in the cumene hydrocracking

1.4 Scope of Study

This study deals with 4 aspects. The first scope covered the preparation of the catalyst. The synthesis of FZSM-5 involved microemulsion system from cetyltrimethyl ammonium bromide (CTAB), toluene, and *n*-butanol. Cationic surfactant, CTAB, was selected due to its ability to form coulombic interaction with silicate gels and zeolite framework (Monnier, *et al.*, 1993). It was also selected because of its structure. Manipulating the packing parameter of single chain surfactant, such as CTAB, was easier due to the absence of steric hindrance. This was proved by Polshetiwar, *et al.* (2010) who discovered the loss of fibrous morphology after using benzalkonium chloride, which is a double chain surfactant. According to Moon and Lee (2012), the co-solvent, which was short-chain alcohol, had important role in controlling the thickness of dendrimeric silica fiber. Their study showed that *iso*-propanol produce thick dendrimer with narrow inter-dendrimer distance and *n*-pentanol produced thin and very wide inter-dendrimer distances. *n*-butanol was chosen as a suitable co-solvent because it produce dendrimer with adequate distance to promote high accessibility. Urea was selected as the hydrolyzing agent for the silica precursor due to its mild basicity. The addition of strong base as hydrolyzing agent, such as NaOH could compromise the microemulsion system. According to the study by Polshettiwar, *et al.* (2010), the addition amount of urea affect the morphology of dendrimeric silica fiber. However, excess addition of urea could increase the particle size of the catalyst due to the rapid hydrolysis of silica precursor. Zeolite crystal-seed crystallization was used instead of direct zeolite crystallization. This was to avoid interaction competition between microemulsion and zeolite structure directing agent and the aluminosilicate species (Li, *et al.*, 2011). The presence of other electrolyte from zeolite precursor, such as Na^+, could changed the critical micelle concentration of CTAB, which will resulted in different formation of supramolecular structure. Thus, zeolite crystal-seed crystallization was best suited to be used in synthesis method to avoid the competition and minimizing the changes in CTAB critical micelle concentration. All catalysts were converted into ammonium form by ion-exchange and followed by calcination to convert the NH_4^+ species into H^+. Platinum was chosen as the metal active species in all catalyst. Platinum metal showed high catalytic activity in hydrocracking regardless the support material (Regali, *et al.*, 2013; Verheyen, *et al.*, 2013). Thus, platinum metal could serve as good example for hydrocracking reaction.

Secondly, the scope is about the characterization of the catalyst. The morphological features of FZSM-5 was examined with Field emission scanning electron microscopy (FESEM). Elemental analysis of FZSM-5 was carried out with energy dispersion X-ray (EDX). The structure of FZSM-5 was characterized with X-ray diffraction (XRD) to confirm the presence of FZSM-5 structure. The surface and pore analysis were obtained by N_2 adsorption-desorption. The surface area was obtained by BET method, pore distribution was obtained by BJH method, and micropore analysis was obtained by *t*-plot method. Molecular vibration of FZSM-5 was assessed with Fourier transform infrared (FTIR) spectroscopy. The acidic properties of FZSM-5 was subjected to pyridine due to its size and ability to access all acid sites both on the surface and inside the pore of catalyst. For comparison purpose, commercial ZSM-5 was also undergo similar characterization.

The catalytic activity of FZSM-5 was assessed with hydrocracking reaction. Hydrocracking could give clear depiction of catalyst catalytic properties with/without any additives (Choudary and Saraf, 1975). Among various of available feedstocks, cumene was selected as the reactant. Cumene hydrocracking was chosen as model reaction due to the fewer amount of complex side reactions. Thus, it will be easier to determine the catalytic activity of a catalyst (Bielanski and Malecka, 1984). The reaction was conducted under a hydrogen stream to maintain the metallic state of platinum and constant supply of molecular hydrogen. For comparison purpose, cumene hydrocracking reaction using commercial ZSM-5 was also conducted.

The fourth and final scope covered the stability studies of FZSM-5. The catalytic reaction was carried out in the temperature range of 423 – 623 K. The maximum reaction temperature was chosen to avoid any bias from the presence of thermal cracking (Greensfelder, *et al.*, 1949). Chen, *et al.* (1977), reported the presence of cracking product at 673 K over fumed silica, which they claimed catalytically inactive. This could be attributed to the presence of thermal cracking. From previous study, only a small fraction of cumene hydrocracking products was observed in the reaction temperature below 373 K and gradually increase after 423 K. (Annuar, *et al.*, 2014; Sazegar, *et al.*, 2012). The stability of FZSM-5 was studied at the optimum reaction temperature, which obtained the highest activity in cumene hydrocracking. The catalytic stability was conducted in 100 doses of cumene.

1.5 Significance of Study

Fibrous ZSM-5 (FZSM-5), protonated FZSM-5 (HFZSM-5), and Pt loaded HFZSM-5 (Pt/HFZSM-5) was prepared in this study as an efficient catalyst in hydrocracking of cumene. The investigation regarding physical and chemical properties of the catalysts had been studied. The fibrous morphology is a novel morphology for ZSM-5. The fibrous morphology would enhance the surface area and active sites accessibility of ZSM-5. FZSM-5 would be a more efficient catalyst to be applied in oil and gas industries due to higher catalytic activity and stability in hydrocracking of cumene compared to ZSM-5.

1.6 Thesis Outline

The study was divided into five chapters. The first chapter consists of the introduction of hydrocracking and their progress on their catalyst. The problem statement and hypothesis of the current research is stated to give a clear objective of current research. There is also scopes of study that will be conducted to meet the objectives.

Chapter 2 covers the literature review and knowledge regarding previous research in hydrocracking process and catalyst, advances in zeolite development, and previous effort and research in silica-based fibrous material development. The background and the concept for developing zeolite-based fibrous material are also covered in this chapter

Chapter 3 comprises of the details regarding materials and chemicals that are used in this research. The complete procedure with experimental setup and analysis for catalyst preparation, characterization, and catalytic testing in hydrocracking of cumene are also included in this chapter.

Chapter 4 contains the results and discussion of the present research. The data are presented and analyzed comprehensively. Finally, chapter 5 covers the conclusion and recommendation for future work and development.

REFERENCES

Aboul-Gheit, A. K., Aboul-Fotouh, S. M. and Aboul-Gheit, N. A. K. (2005). Hydroconversion of Cyclohexene Using Catalysts Containing Pt, Pd, Ir and Re Supported on H-ZSM-5 Zeolite. *Applied Catalysis A: General*. 283(1-2): 157-164.

Aboul-Gheit, A.K., Awadallah, A.E., El-Desouki, D.S., Aboul-Gheit, N.A.K. (2009). *n*-pentane Hydroconversion Using Pt-loaded Zeolite Catalysts. *Petroleum Science and Technology*. 27: 2085-2096.

Acheyta. J., Sanchez. S., and Rodriguez. M.A. (2005). Kinetic Modeling of Hydrocracking of Heavy Oil Fractions: A Review. *Catalysis Today.* 109:76-92

Afanasiev, P., Geantet, C., Breysse, M., Coudurier, G., and Vedrine, J.C. (1994). Influence of Preparation Method on the Acidity of MoO3 (WO3)/ ZrO2 Catalysts. *Journal of the Chemical Society, Faraday Transactions.* 90: 193-202.

Al-Khattaf, S., de Lasa, H. (2002). The Role of Diffusion in Alkyl-benzene Catalytic Cracking. *Applied Catalysis A: General*. 226: 139-153

Annuar. N.H.R., Jalil, A.A., Triwahyono, S., Fatah, N.A.A., Teh, L.P., Mamat, C.R. (2014). Cumene Cracking over Chromium Oxide Zirconia: Effect of Chromium (VI) Oxide Precursors. *Applied Catalysis A: General*. 475: 487-496.

Auerbach, S.M., Carrado, K.A., Dutta, P.K. (2003). *Handbook of Zeolite Science and Technology.* 1st edition. Marcel Dekker Inc: New York

Batalha, N., Pinard, L., Bouchy, C., Guillon, E., Guisnet, M. (2013). n-Hexadecane hydroisomerization over Pt-HBEA catalysts. Quantification and effect of the intimacy between metal and protonic sites. *Journal of Catalysis*. 307: 122-131

Baerlocher. Ch., McCusker. L.B., Olson. D.H. (2007). *Atlas of Zeolite Framework Types*. Elsevier: Netherlands.

Belhakem, A., Benguedach, A. (2005). Cumene Cracking on Modified Mesoporous Material Type MCM-41. *Turkey Journal of Chemistry*. 30: 187 – 195.

Bekkum, H., Flanigen, E. M., Jacobs, P. A. and Jansen, J. C. (2001). *Introduction to Zeolite Science and Practice.* (2nd ed.). Amsterdam: Elsevier.

Bielandski, A., Malecka, A. (1984). Cumene Cracking on NaH-Y and NaH-ZSM-5 Type Zeolites as Catalysts. *Zeolites.* 6: 249 – 253.

Breck, D.W. (1974). *Zeolit Molecular Sieves*. John Wiley and Sons Ltd: New York.

Buzzoni, R., Bordiga, S., Ricchiardi, G., Lamberti, C., Zecchina A. (1996). Interaction of Pyridine with Acidic (H-ZSM-5 H-β, H-MORD Zeolites) and Superacidic (H-Nafion Membrane) Systems: An IR Investigation. *Langmuir*. 12: 930-940

Campbell, D.R., and Wociechowski, B.W. (1971). Catalytic Cracking of Cumene on Aging Catalysts. I. The Mechanism of the Reaction. *Journal of Catalysis*. 20: 217-222.

Campelo, J.M., Lafont, F., Marinas, J.M. (1998). Hydroconversion of *n*-Dodecane over Pt/SAPO-11 Catalyst. *Applied Catalysis A: General.* 170: 139-144.

Cavani, F., Trifiro, F. (1997). Classification of Industrial Catalysts and Catalysis for the Petrochemical Industry. *Catalysis Today*. 34:269-279

Chen, N.Y., Mitchell, T.O., Olson, D.H., Pelrine, B.P. (1977). Irreversible Deactivation Of Zeolite. 2. Hydrothermal Stability of Catalysts Containing NH_4Y and Rare Earth Y. *Industrial & Engineering Chemistry Product Research and Development.* 16: 247-252.

Choudary, N., Saraf, D.N., (1975). Hydrocracking: A Review. *Industrial and Engineering Chemistry. Product Research Development.* 14: 74-83.

Corma, A and Wojciechowski, B.W. (1982). The Catalytic Cracking of Cumene. *Catalysis Reviews: Science and Engineering*. 24: 1- 65

Corma, A. (1997). From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chemical Reviews.* 97: 2373-2419

Corma, A. and Martinez, A. (2005). Zeolites in Refining and Petrochemistry. *Studies in Surface Science and Catalysis.* 157: 337-366.

Cruz-Cabeza, A.J., Esquivel, D., Jimenez-Sanchidrian, C., Romero-Salguero, F.J. (2012). Metal-exchanged β Zeolites as Catalysts for the Conversion of Acetone to Hydrocarbon. *Materials*. 5: 121-134.

De Rossi, S., Casaletto, M.P., Ferraris, G., Cimino, A. and Minelli, G. (1998). Chromia/Zirconia Catalysts with Cr Content Exceeding the Monolayer. A Comparison with Chromia/Alumina and Chromia/Silica for Isobutane Dehydrogenation. *Applied Catalysis A: General.* 167: 257-270.

Degnan. T.F. (2003). The Implication of the Fundamentals of Shape Selectivity for the Development of Catalysts for the Petroleum and Petrochemical Industries. *Journal of Catalysis.* 216:32-46

Dessau, R.M. (1990). Base- and Acid-catalyzed Cyclization of Diketones over ZSM-5. *Zeolites*. 10: 205-206

Egeblad, K., Christensen, C.H., Kustova, M., Christensen, C.H. (2008). Templating Mesoporous Zeolites. *Chemistry Material*. 20: 946-960

Fihri, A., Cha, D.., Bouhrara, M., Almana, N., Polshettiwar, V. (2012). Fibrous Nano-silica (KCC-1)-Supported Palladium Catalyst: Suzuki Coupling Reactions under Sustainable Conditions. *ChemSusChem.* 5: 85-89.

Fincy, P. and Sugunan, S. (2011). Cracking of Cumene on Tungsten Promoted Ceria Catalysts. *Reaction Kinetic, Mechanisms and Catalysis*. 103:125–131.

Fujimoto, K., Maeda, K. and Aimoto, K. (1992). Hydroisomerization of *n*-Pentane over Hybrid Catalysts Containing a Supported Hydrogenation Catalyst. *Applied Catalysis A: General*. 91(2): 81-86.

Greensfelder, B.S., Voge, H.H., Good, G.M. (1949). Catalytic and Thermal Cracking of Pure Hydrocarbon: Mechanisms of Reaction. *Industrial Engineering Chemistry.* 41: 2573-2584.

Guo, Q., Chen, B., Li, Y., Li, J. (2008). The Effect of Different Active Sites on the Catalytic Activity of Fe-ZSM-5 Zeolite for N_2O Direct Decomposition. *Catalysis Letters*. 120:65-70

Gutierrez, A., Arandes, J.M., Castano, P., Olazar, M., Barona, A., Bilbao, J. (2012). Effect of Space Velocity on the Hydrocracking of Light Cycle Oil over a Pt-Pd/HY zeolite. *Fuel Processing Technology*. 95: 8-15

Han, J., Wang, X., Yue, J., Gao, S., Xu, G. (2014). Catalytic Upgrading of Coal Pyrolysis Tar over Char-based Catalysts. *Fuel Processing Technology*. 122: 98

Hart, A. (2013). A Review of Technologies for Transporting Heavy Crude Oil and Bitumen via Pipeline. *Journal of Petroleum Exploration and Production Technology*. 4:327-336.

Hattori, H. and Shishido, T. (1997). Molecular Hydrogen-Originated Protonic Acid Sites as Active Site on Solid Acid Catalyst. *Catalysis Surveys from Japan.* 1(2): 2005-213.

Hattori, H. (2001). Molecular Hydrogen-Originated Protonic Acid Site. *Studies in Surface Science and Catalysis*. 138: 3-12

Hattori, H. (2010). Solid Acid Catalysts: Roles in Chemical Industries and New Concepts. *Topics in Catalysis*. 53(7-10): 432-438

Henrich, V.E., and Cox, P.A. (1993). Fundamentals of Gas-Surface Interactions on Metal Oxides. *Applied Surface Science.* 72: 277-284

Iyoki, K., Kamimura, Y., Itabashi, K., Shimojima, A., Okubo, T. (2010). Synthesis of MTW-type Zeolites in the Absence of Organic Structure-Directing Agent. *Chemistry Letter*. 39:730-731.

Jana, S.K., Takahashi, H., Nakamura, M., Kaneko, M., Nishida, R., Shimizu, H., Kugita, T., Namba, S. (2003). Aluminum Incorporation in Mesoporous MCM-41 Molecular Sieves and Their Catalytic Performance in Acid-catalyzed Reactions. *Applied Catalysis A: General*. 245: 33-41.

Janiszewska, E., Macario, A., Wilk, J., Aloise, A., Kowalak, S., Nagy, J.B., Giordano, G. (2013). The Rle of Defect Groups on the Silicalite-1 Zeolite Catalytic Behaviour. *Microporous and Mesoporous Materials.* 182: 220-228

Kasahara, S., Itabashi, K., Igawa, K. (1986). Clear Aqueous Nuclei Solution for Faujasite Synthesis. *Studies in Surface Science and Catalysis*. 28: 185-192.

Khatamian, M., Khandar, A.A., Haghighi, M., Ghadiri, M. (2011). Nano ZSM-5 Type Ferrisilicates as Novel Catalysts for Ethylbenzene Dehydrogenation in the Presence of N_2O. *Applied Surface Science*. 258: 865-872

Kondo, J.N., Nishitani, R., Yoda, E., Yokoi, T., Tatsumi, T., Domen, K. (2010). A Comparative IR Characterization of Acidic Sites on HY Zeolite by Pyridine and CO Probes with Silica-Alumina and γ-alumina References. *Physical Chemistry Chemical Physics*. 12. 11576

Kong, C., Lu, J., Yang, J., Wang, J. (2007). Catalytic Dehydrogenation of Ethylbenzene to Styrene in a Zeolite Silicalite-1 Membrane Reactor. *Journal of Membrane Science*, 306: 29-35.

Konno, H., Tago, T., Nakasaka, Y., Watanabe, G., Masuoka, T. (2011). Characterization and Catalytic Performance of Modified Nano-scale ZSM-5 for the Acetone-to-Olefins Reaction. *Applied Catalysis A: General*, 475: 127-133.

Koo, J-B., Jiang, N., Saravanamurugan, S., Bejblova, M., Musilova, Z., Cejka, J., Park, S-E. (2010). Direct Synthesis of Carbon-templating Mesoporous ZSM-5 using Microwave Heating. *Journal of Catalysis.* 276:327-334.

Kosslick, H., Landmesser, H., Fricke, R. (1997). Acidity of Substituted MCM-41-type Mesoporous Silica Probed by Ammonia. *Journal of the Chemical Society, Faraday Transactions*. 93: 1849-1854.

Kubo. K., Iida. H., Namba. S., and Igarashi. A. (2012). Ultra-high Steaming Stability of Cu-ZSM-5 Zeolite as Naphtha Cracking Catalyst to Produce Light Olefin. *Catalysis Communications*. 29: 162-165

Kubota, Y., Helmkamp, M.M., Zones, S.I., Davis, M.E. (1996). Properties of Organic Cations That Lead to the Structure-direction of High-silica Zeolite. *Microporous and Mesoporous Materials*. 6: 213-229

Kweon, H., Ngyen-Huy, C., Kim, H., Lee, Y., Shin, E.W. (2014). Coking Behavior on a Ni-Mo/Al_2O_3 Catalyst for the Hydrocracking of Vacuum Residue. *Reaction Kinetics, Mechanisms and Catalysis*. 113: 133-147.

Le, X., Dong, Z., Zhang, W., Li, X., Ma, J. (2014). Fibrous Nano-silica Containing Immobilized Ni@Au Core-shell Nanoparticles: A Highly Active and Reusable Catalyst for The Reduction of 4-nitrophenol and 2-nitroaniline. *Journal of Molecular Catalysis A: Chemical*. 395: 58-65.

Lee, S., Shantz, D.F. (2005). Zeolite Growth in Nonionic Microemulsions: Synthesis of Hierarchically Structured Zeolite Particles. *Chemistry Material*. 17: 409-417

Lercher, J.A., and Jentys, A. (2007). Chapter 13 Infrared and Raman Spectroscopy for Characterizing Zeolites. *Studies in Surface Science and Catalysis*. 168: 435-476.

Li, H., Wu, H., Shi, J. (2013). Competition Balance Between Mesoporous Self-assembly and Crystallization of Zeolite: A Key to the Formation of Mesoporous Zeolite. *Journal of Alloys and Compound*. 566: 71-78

Li, J., Miao, P., Li, Z., He, Z., He, T., Han, D., Wu, J., Wang, Z., Wu, J. (2015). Hydrothermal Synthesis of Nanocrystalline H[Fe,Al]ZSM-5 Zeolites for Conversion of Methanol to Gasoline. *Energy Conversion and Management.* 93: 259-266.

Liu, X. (2009). Chapter 5 Infrared and Raman Spectroscopy. *Zeolite Characterization and Catalysis*. Springer. New York.

Maesen, T.L.M., Calero, S., Schenk, M., Smith, B. (2004). Alkane Hydrocracking: Shape Selectivity or Kinetics?. *Journal of Catalysis*. 221: 241 – 251.

Mahgoub, K.A., Al-Khattaf, S. (2005). Catalytic cracking of Hydrocarbons in a Riser Simulator: The Effect of Catalyst Accessibility and Acidity. *Energy Fuels.* 19: 329-338.

Majhi, S., Dalai, A.K., Pant, K.K. (2015). Methanol Assisted Methane Conversion for Higher Hydrocarbon Over Bifunctional Zn-modified Mo/HZSM-5 Catalyst. *Journal of Molecular Catalysis A: Chemical*. 398: 368-375.

Marcilly. C.R. (2000). Where and How Shape Selectivity of Molecular Sieves Operates in Refining and Petrochemistry Catalytic Processes. *Topic in Catalysis*. 2000. 13:357-366

Matsuda, T., Fuse, T. and Kikuchi, E. (1987). The Effect of Spilled-over Hydrogen on the Activity of Montmorillonite Pillared by Aluminum Oxide for Conversion of Trimethylbenzenes. *Journal of Catalysis*. 106: 38-46.

Mediavilla. M., Melo. L., Brito. J. L., Moronta. D., Solano. R., Gonzalez. (2013). I. Synthesis of Pt and Pt–Sn Catalysts Supported on H-Y Zeolite Induced by Microwave Radiation. *Microporous and Mesoporous Materials*. 170:189-193

Meng. X., Nawaz. F., Xiao. F-S. (2009). Templating Route for Synthesizing Mesoporous Zeolites with Improved Catalytic Properties. *Nano Today*. 4: 292-301.

Meng, X., Xiao, F-S. (2014). Green Routes for Synthesis of Zeolites. *Chemical Reviews*. 114: 1521-1543.

Mintova, S. and Cejka, J., (2007), Micro/Mesoporous Composites – Introduction to Zeolite Science and Practice 3rd Ed, *Elsevier.* 301-326.

Monnier, A., Schuth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R.S., Stucky, G.D., Krishnamurty, M., Petroff, P., Firouzi, A., Janicke, M., Chmelka, B.F. (1993). Cooperative Formation of Indorganic-Organic Interfaces in the Synthesis Silicate Mesostructures. *Science.* 261: 1299-1303.

Moon, D-S., Lee, J-K. (2012). Tunable Synthesis of Hierarchical Mesoporous Silica Nanoparticles with Radial Wrinkle Structure. *Langmuir.* 28: 12341-12347.

Moran, C., Gonzalez, E., Sanchez, J., Solano, R., Carruyo, G., Moronta, A. (2007). Dehydrogenation of Ethylbenzene to Styrene using Pt/Mo.Pt-Mo Catalysts Supported on Clay nanocomposites. *Journal of Colloid and Interface Science.* 315: 164-169

Nie, Y., Shang, S., Xu, X., Hua, W., Yue, Y., Gao, Z. (2012). In_2O_3-doped $Pt/WO_3/ZrO_2$ as a Novel Efficient Catalyst for Hydroisomerization of *n*-heptane. *Applied Catalysis A: General.* 433: 69-74

Padro, C.L., Rey, E.A., Gonzalez, P., Apesteguia, C.R. (2011). Activity, Selectivity, and Stability of Zn-exchanged NaY and ZSM-5 Zeolites for The Synthesis of o-hydroxyacetophenenone by Phenol Acylation. *Microporous and Mesoporous Materials*. 143: 236-242.

Peeters, E., Cattenot, M., Geantet, C., Breysse, M., Zotin, J.L. (2008). Hydrodenitrogenation on Pt/silica-alumina Catalysts in the Presence of H_2S: Role of Acidity. *Catalysis Today.* 133: 299-304

Polshettiwar, V., Cha, D., Zhang, X., Basset, J.M. (2010). High-surface-area Silica Nanosphere (KCC-1) With a Fibrous Morphology. *Angewandte Chemie*. 49: 9652-9656.

Primo. A., and Garcia. H. (2014). Zeolites as Catalysts in Oil Refining. *Chemical Society Review*. 433:7548

Pudukudy, M., Yaakob, Z., Akmal, Z.S. (2015). Direct Decomposition of Methane Over SBA-15 Supported Ni, Co, and Fe Based Bimetallic Catalysts. *Applied Surface Science*. 330: 418-430.

Rahman, M.A., Azad, M.A.K., Ahsan, S., Islam, S., Motin, M.A. and Asadullah, M. (2006). Measurement of Brönsted Acidity of Silica-Alumina Solid Catalyst by Base Exchange Method. *Journal of Surface Science and Technology*. 22: 25-33.

Reddy, B.M., and Reddy, V.R. (2000). Influence of $SO4^{2-}$, Cr_2O_3, MoO_3, and WO_3 on the on Stability of ZrO^{2-} Tetragonal Phase. *Journal of Materials Science Letters.* 19: 763-765.

Regali, F., Boutonnet, M., Jaras, S. (2013). Hydrocracking of n-hexadecane on Noble Metal/Silica-alumina Catalysts. *Catalysis Today*. 214: 12-18

Schneider, J., Mastelaro, V.R., Panepucci, H., Zanotto, E.D. (2000). ^{29}Si MAS-NMR Studies of Q^n Structural Units in Metasilicate Glasses and Their Nucleating Ability. *Journal of Non-Crystalline Solids*. 273: 8-18.

Sazegar, M.R., Jalil, A.A., Triwahyono, S., Mukti, R.R., Aziz, M., Aziz, M.A.A., Setiabudi, H.D., Kamarudin, N.H.N. (2014). Protonation of Al-grafted Mesostructured Silica Nanoparticles (MSN): Acidity and Catalytic Activity for Cumene Conversion. *Chemical Engineering Journal*. 240: 352-361.

Schmidt, F., Lohe, M.R., Buchner, B., Giordanino, F., Bonino, F., Kaskel, S. (2013). Improved Catalytic Performance of Hierarchical ZSM-5 Synthesized by Desilication with Surfactant. *Microporous and Mesoporous Materials.* 165: 148-157.

Selli, E. and Forni, L. (1999). Comparison between the Surface Acidity of Solid Catalysts Determined by TPD and FTIR Analysis of Pre-adsorbed Pyridine *Microporous Mesoporous Material.* 31:129–140.

Seo. M-G., Lee. D-W., Lee. K-Y., and Moon. D.J. (2014). Pt/Al-SBA-15 Catalysts for Hydrocracking of C_{21}-C_{34} *n*-paraffin Mixture into Gasoline and Diesel Fractions. *Fuel.* 143: 63-71

Serrano, D.P., Escola, J.M., Pizarro, P. (2013). Synthesis Strategies in the Search for Hierarchical Zeolites. *Chemical Society Reviews*. 42: 4004-4035.

Setiabudi, H.D., Triwahyono, T., Jalil, A.A., Kamarudin, N.H.N, Aziz, M.A.A. (2011). Effect of Iridium Loading on HZSM5 for Isomerization of *n*-Heptane. *Journal of Natural Gas Chemistry.* 20: 477-482.

Setiabudi, H.D., Jalil, A.A., Triwahyono, S., Kamarudin, N.H.N., Mukti, R.R. (2012). IR Study of Iridium Bonded to Perturbed Silanol Groups of Pt-

HZSM5 for *n*-pentane isomerization. *Applied Catalysis A: General*. 417: 190-199

Shafiee. S., and Topal. E. (2009). When Will Fossil Fuel Reserves be diminished? *Energy Policy*. 37:181-189

Shishido. T., and Hattori. H. (1995). Hydrogen Effects on Cumene Cracking over Zirconium Oxide Promoted by Sulfate Ion and Platinum. *Journal of Catalysis*. 161:194-197

Shpiro, E.S., Grunert, W., Joyner, R.W., Baeva, G.N. (1994). Nature, Distribution and Reactivity of Copper Species in Over-exchanged Cu-ZSM-5 Catalysts: an XPS/XAES Study. *Catalysis letters.* 1: 159.

Silaghi, M-C., Chizallet, C., Raybaud, P. (2014). Challenges on Molecular Aspects of Dealumination and Desilication of Zeolites. *Microporous and Mesoporous Materials.* 191: 82-96.

Sun, A., Qin, Z., Wang, J. (2002). Reaction Coupling of Ethylbenzene Dehydrogenation with Water-gas Shift. *Applied Catalysis A: General*. 234: 179-189.

Szanyi, J., Paffeti, M.T. (1996). The Adsorption of Carbon Monoxide on H-ZSM-5 and Hydrothermally Treated H-ZSM-5. *Microporous Materials*. 7: 201-218.

Tanabe, K., Misono, M., Ono, Y., and Hattori, H. (1989). *New Solid Acids and Bases. Their Catalytic Propertie*s. Amsterdam: Elsevier.

Tao, Y., Kanoh, H., Abrams, L., Kaneko, K. (2006). Mesopore-Modified Zeolites: Preparation, Characterization, and Application. *Chemical Reviews*. 106: 896-910.

Teh, L.P., Triwahyono, S., Jalil, A.A., Mukti, R.R., Aziz, M.A.A., Shishido, T. (2015). Mesoporous ZSM5 Having Both Intrinsic Acidic and Basic Sites for Cracking and Methanation. *Chemical Engineering Journal*. 270: 196-204.

Teh L.P., Triwahyono, S., Jalil, A.A., Mamat C.R., Sidik, S.M., Fatah, N.A.A., Mukti, R.R., Shishido, T. (2015) Nickel-promoted Mesoporous ZSM5 for Carbon Monoxide Methanation. *RSC Advances*. 5: 64651.

Treacy, M.M.J., and Higgins, J.B. (2001). *Collection of Simulated XRD Powder Patterns for Zeolite* 4th edition. Elsevier: Amsterdam.

Triwahyono, S., Yamada, T. and Hattori, H. (2003). IR Study of Acid Sites on WO3-ZrO2 and Pt/WO3-ZrO2. *Applied Catalysis A: General.* 242(1): 101-109

Triwahyono, S., Abdullah, Z. and Jalil, A.A. (2006). The effect of Sulfate Ion on The Isomerization of *n*-Butane to iso-Butane. *Journal of Natural Gas Chemistry*. 15(4): 247-252.

Triwahyono, S., Jalil, A.A., Hattori, H. (2007). Study of Hydrogen Adsorption on Pt/WO_3-ZrO_2 through Pt Sites. *Journal of Natural Gas Chemistry*. 16: 252-257.

Triwahyono, S., Jalil, A.A., Mukti, R.R., Musthofa, M., Razali, N.A.M., Aziz, M.A.A. (2011). Hydrogen Spillover Behavior of Zn/HZSM-5 Showing Catalytically Active Protonic Acid Sites in Isomerization of *n*-pentane. *Applied Catalysis A: General*. 407: 91-99

Todorova, S., Su, B-L. (2003). Propane as Alkylating Agent for Benzene Alkylation on Bimetal Ga and Pt Modified H-ZSM-5 Catalysts: FTIR Study of Effect of Pre-treatment Conditions and the Benzene Adsorption. *Journal of Molecular Catalysis A: Chemical*. 201: 223-235.

Topsoe, N.Y., Pedersen, K., Derouane, E.G. (1981). Infrared and Temperature-programmed Desorption Study on acidic Properties of ZSM-5-type Zeolites. *Journal of Catalysis.* 70: 41-52.

Uytterhoeven, J.B., Christner, L.G., Hall, W.K. (1965). Studies of the Hydrogen Held by Solids. VIII. The Decationed Zeolites. *Journal of Physical Chemistry.* 69: 2117-2126.

Verhayen, E., Jo, C., Kurttepeli, M., Vanbutsele, G., Gobechiya, E., Koranyi, T.I., Bals, S., Tendeloo, G.V., Ryoo, R., Kirschhock, C.E.A., Martens, J.A. (2013).Molecular Shape-selectivity of MFI Zeolite Nanosheets in *n*-decane Isomerization and Hydrocracking. *Journal of Catalysis*. 300: 70-80.

Villegas, J.I., Kumar, N., Heikkila, T., Lehto, V-P., Salmi, T., Murzin, D.Y. (2006). Isomerization of *n*-butene to isobutene over Pt-modified Beta and ZSM-5 Zeolite Catalysts: Catalyst Deactivation and Regeneration. *Chemical Engineering Journal.* 120: 83-89

Vora, B.V. (2012) Development of Dehydrogenation Catalysts and Processes. *Topics in Catalysis.* 55: 1297-1308.

Vu, X.H., Bentrup, U., Hunger, M., Kraehnert, R., Armbuster, U., Martin, A. (2014). Direct Synthesis of Nanosized ZSM-5/SBA-15 Analog Composites from

Preformed ZSM-5 Precursors for Improved Catalytic Performance as Cracking Catalyst. *Journal of Material Science.* 49: 5676-5689.

Warzywoda, J., Edelman, Edelman, R.D., Thompson, R.W. (1991). Crystallization of High-silica ZSM-5 in the Presence of Seed. *Zeolites*. 4:318-324.

Weyda, H., and Kohler, E. (2003). Modern Refining Concepts – An Update on Naphtha-Isomerization to Modern Gasoline Manufacture. *Catalysis Today*. 81: 51-55.

Winsor, P.A. (1948) Hydrotropy, Solubilisation and Related Emulsifications Processes, Part I. *Transaction of the Faraday Society*. 44: 376-398

Xiang. C., Yang. G., Wu. M., Yang. R., Tang. L., Zhu. P., Wei. Q., Li. J., Mao. J., Yoneyama. Y., and Tsubaki. N. (2015). Hierarchical Zeolite Y Supported Cobalt Bifunctional Catalyst for Facilely Tuning the Product Distribution of Fischer-Tropsch Synthesis. *Fuel*. 148:48-57

Xie, Y., Sharma, K.K., Anan, A., Wang, G., Biradar, A.V. and Asefa, T. (2009). Efficient Solid-Base Catalysts for Aldol Reaction by Optimizing the Density and Type of Organoamine Groups on Nanoporous Silica. *Journal of Catalysis*. 265:131–140.

Xie, B., Zhang, H., Yang, C., Liu, S., Ren, L., Zhang, L., Meng, X., Yilmaz, B., Muller, U., Xiao, F-S. (2011). Seed-directed Synthesis of Zeolites with Enhanced Performance in the Absence of Organic Templates. *Chemical Communications*. 47: 3945-3947

Xing, C., Yang, G., Wu, M., Yang, R., Tan, Li., Zhu, P., Wei, Q., Li, J., Mao, J., Yoneyama, Y., Tsubaki, N. (2015). Hierarchical Zeolite Y Supported Cobalt Bifunctional Catalyst Facilely Tuning the Product Distribution of Fischer-Tropsch Synthesis. *Fuel*. 148: 48-57.

Xu, X., Liu, T., Xie, P., Yue, Y., Miao, C., Hua, W., Gao, Z. (2014). Enhanced Catalytic Performance over Fe_2O_3-doped $Pt/SO_4^{2-}/ZrO_2$ in n-heptane Hydroisomerization. *Applied Catalysis A: General.* 433: 69-74.

Yang, C., Zhang, J., Xu, C., Lin, S. (1998). Hydroconversion Characteristics on Narrow Fractions of Residua. *ACS Division of Fuel Chemistry.* 43:746-750.

Yashiki, A., Honda, K., Fujimoto, A., Shibata, S., Ide, Y., Sadakane, M., Sano, T. (2011). Hydrothermal Conversion of FAU Zeolite into LEV Zeolite in the

Presence of non-calcined Seed Crystals. *Journal of Crystal Growth*. 325: 96-100.

Yin, C., Feng, L., Ni, R., Hu, L., Zhao, X., Tian, D. (2014). One-pot Synthesis of Hierarchically Nanoporous ZSM-5 for Catalytic Cracking. *Powder Technology*. 253: 10-13

Yeu, Y., Gedeon, A., Bonardet, J.L, D'Espinose, J.B., Fraissard, J., Melosh, N. (1999). Direct Synthesis of Al-SBA Mesoporous Molecular Sieves: Characterization and Catalytic Activities. *Chemical Communication.* 1967-1968.

Zana, R. (2005). *Dynamics of Surfactant Self-Assemblies.* CRC Press: NW USA.

Zhang, X., Zhang, F., Yan, X., Zhang, Z., Sun, F. (2014). Hydrocracking of Heavy Oil Using Zeolites Y/Al-SBA-15 Composites as Catalysts Supports. *Journal of Porous Materials.* 15: 145

Zhao, Q., Qin, B., Zheng, J., Du, Y., Sun, W., Ling, F., Zhang, X., Li, R. (2014). Core-shell Structured Zeolite-Zeolite Composites Comprising Y Zeolite Cores and Nano-β shells: Synthesis and Application in Hydrocracking of VGO Oil. *Chemical Engineering Journal*. 257: 262-272.

Zhao, L., Qin, H., Wu, R., Zou, H. (2012). Recent Advances of Mesoporous Materials in Sample Preparation. *Journal of Chromatography A.* 1228: 193-204.

Zhao. Y., Lin. X., and Li. D. (2014). Catalytic Hydrocracking of a Bitumen Derived Ashpaltene over NiMo/γ-Al_2O_3 at Various Temperature. *Chemical Engineering and Technology*. 38:297-303