representative from DDC to discuss donation of an engine control interface that would permit access to the engine control parameters. If this donation can be arranged, we would have the capability to perform precise experiments on the impact of the coal-derived fuel compounds on emissions by maintaining control on engine operation parameters such as EGR rate and injection timing.

Task 3. Desulfurization, Denitrogenation, Saturation of Aromatics, Chemicals from Coal

(Chunshan Song, Xiaochun Xu, Jae Hyung Kim, Brian Senger and Xiaoliang Ma)

This work relates to the integrated refinery processing of RCO and LCO for production of ultra-clean diesel fuels and for making value-added industrial aromatic chemicals. RCO is rich in naphthalene and also contains some nitrogen compounds such as quinoline. LCO is also rich in naphthalene structures but contains refractory sulfur compounds such as 4,6-dimethyldibenzothiophene.

This task deals with the following three subtasks, (1) deep desulfurization and denitrogenation, because LCO has a higher content of refractory sulfur compounds while RCO has a higher content of nitrogen compounds; (2) dearomatization of two-ring compounds, because both RCO and LCO are rich in aromatic structures; and (3) shape-selective conversion of naphthalene into 2,6-dimethylnaphthalene, because both RCO and LCO compositions are dominated by naphthalene structures, and a small fraction of them could be used for making value-added industrial chemicals.

Subtask 3.1: Desulfurization and Denitrogenation

As a part of the DOE refinery integration project, this sub-task aims at more effective deep desulfurization for obtaining ultra-clean diesel fuels which contain below 15 ppmw sulfur. For this purpose, the refractory sulfur compounds, particularly 4,6-dimethyldibenzothiophene (4,6-DMDBT), must be desulfurized or removed. General approaches to deep hydrodesulfurization include 1) improving the catalytic activity of the molybdenum sulfide-based catalysts used in the refining industry [26,27]; 2) developing new catalysts [28-30]; 3) tailoring reaction and process conditions [31], and 4) designing new reactor configurations [31]. In general, deep hydrodesulfurization of dibenzothiophenes over heterogeneous catalysts proceeds through two reaction pathways. One is hydrogenation (HYD) pathway, involving aromatic ring saturation and the other is a hydrogenolysis pathway via C-S bond cleavage, which is also called the direct desulfurization (DDS) pathway [32,33].

Figure 5 shows a schematic diagram for 4,6-DMDBT HDS showing hydrogenation/hydrogenolysis pathways [34]. To understand deep hydrodesulfurization mechanism and develop new type deep HDS catalysts, it is necessary to investigate the HDS activity kinetically for both reaction pathways (HYD and DDS pathways) as well as for overall reaction [34,35].
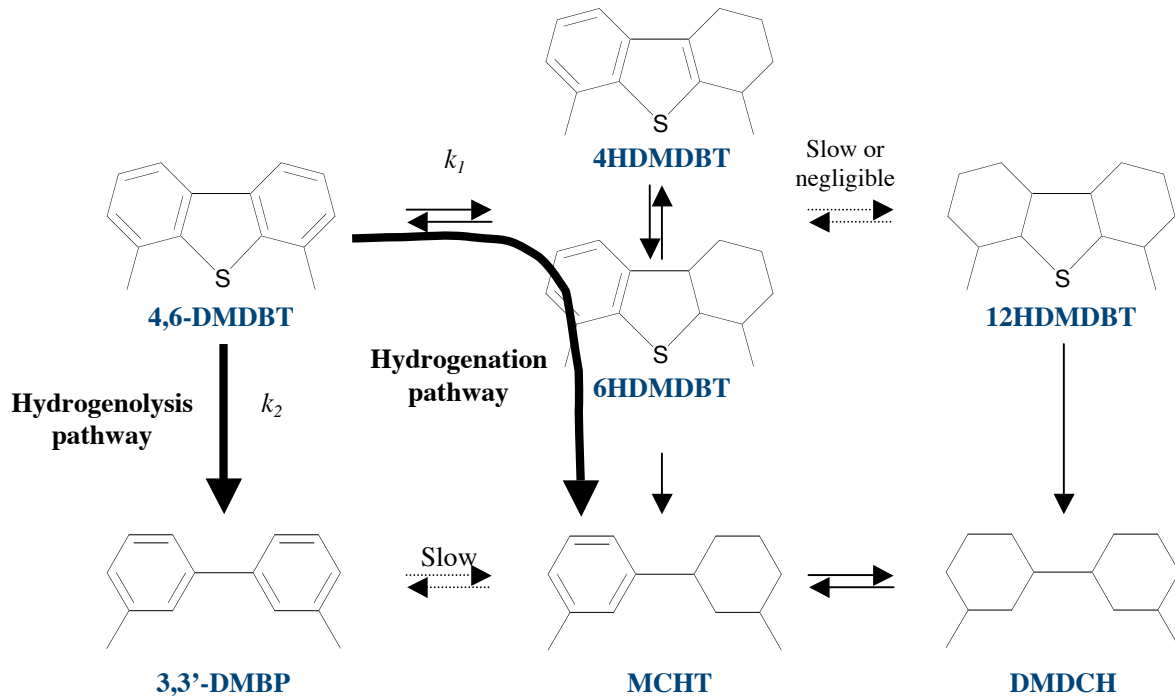
4HDMDBT

Slow or negligible

k_1

4,6-DMDBT

12HDMDBT

Hydrogenation pathway

6HDMDBT

Hydrogenolysis pathway k_2

Slow

3,3'-DMBP

MCHT

DMDCH

Figure 5. Scheme of 4,6-DMDBT HDS via ring hydrogenation (k_1) and direct C-S bond hydrogenolysis (k_2) pathways.

For production of clean fuels with low sulfur level, the effects of inhibitors, especially aromatic and nitrogen compounds, should be also considered and investigated. Recent study has indicated that some aromatic and nitrogen compounds present in the feed inhibit deep desulfurization significantly when the sulfur in feed is dropped to below 500 ppm level, since the aromatic and nitrogen compounds can compete with sulfur compounds on catalyst surface [36, 37].

3.1.1. Experimental

The reactant chemicals, 4,6-DMDBT, DBT, and decahydronaphthalene (decalin, used as solvent), were obtained from Aldrich Chemical Co. and were used without

further purification. For the HDS of 4,6-DMDBT, its concentration was 1.23 wt% (0.81 mol%) in decalin. In order to examine the effect of aromatic compounds on HDS of 4,6-DMDBT, an equimolar amount of 1-methylnaphthalene (1-MN) and 4,6-DMDBT (or 0.74 mol of fluorene and 1.00 mol of 4,6-DMDBT) were added into the feed. For examination of nitrogen compound effect, 150 ppmw N (0.14 wt% quinoline) was added into the feed.

HDS was carried out in a batch reactor with a volume of 25 ml. The reactor was loaded with 0.1 g catalyst and 4.0 g decalin fuel containing 4,6-DMDBT or DBT, and was then purged with nitrogen and hydrogen five times, respectively, before being pressurized with hydrogen to the desired initial pressure. The reactor was placed in a fluidized sand bath, which was preheated to the desired temperature, and was agitated at 200 strokes/min. The temperature inside the reactor was monitored by a thermocouple. Following the reaction, the reactor was removed from the sand bath and was immediately quenched in a cold-water bath. A GC-MS (Shimadzu GC17A/QP-500) was used for identification of the products, while a gas chromatograph (SRI 8610C), equipped with an FID detector, was used for quantitative analysis of products.

Two commercial catalysts, $CoMo/Al_2O_3$ (Cr344) and $NiMo/Al_2O_3$ (Cr424), obtained from the Criterion Catalyst Co., were used for the HDS of 4,6-DMDBT and DBT. The chemical composition and textural properties of these catalysts are shown in **Table 6.** These two catalysts contained around 15 wt% MoO_3 and 3 wt% NiO or CoO. The $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts had surface areas of 190 and 155 m^2/g, and pore volumes of 0.56 and 0.45 cm^3/g, respectively. NiMo catalysts were also prepared on mesoporous molecular sieve MCM-41, and gamma-alumina with two-step impregnation

method. High metal loaded NiMo catalysts contained around 40 wt% MoO_3 and 11 wt% NiO, and low metal loaded one did around 14 wt% MoO_3 and 3 wt% NiO which are the traditional metal amounts for commercial CoMo or NiMo catalysts.

Table 6. Composition and properties of CoMo and NiMo sulfide and Ni phosphide catalysts

Catalyst	Content (wt%)		Support	Surface area (m^2/g)	Pore volume (cm^3/g)	Density (cm^3/g)	Active sites (_mol/g)
	MoO_3	Co or Ni					
Cr344	13.5 (9.0)	2.9 CoO	Al_2O_3	183.3	0.48	0.74	85.9[a]
Cr424	13.0 (8.7)	3.0 NiO	Al_2O_3	163.2	0.40	0.81	95.0[a]

[a] Measured by oxygen chemisorption

The catalysts were presulfided at 350 °C for 4 h in a flow of 5 vol % H_2S-H_2 at a flow rate of 200 ml/min and were subsequently stored in decalin to minimize oxidation. Irreversible O_2 uptake measurement was carried out to estimate the number of active sites on the sulfide and phosphide catalysts, respectively. After pretreatment of the catalysts, calibrated pulses of O_2 in a He carrier flowing at 26.7 micromol/s (40cm^3 NTP min^{-1}) were injected at room temperature through a sampling valve and the mass 32 (O_2) signal was monitored with a mass spectrometer.

3.1.2. Results and Discussion

3.1.2.1 The effect of nitrogen compound on 4,6-DMDBT HDS

In order to get better kinetic data, the conversion of 4,6-DMDBT was kept below 20%. The main products from 4,6-DMDBT HDS were HDMDBT (hydrodimethyldibenzothiophene), MCHT (methyl cyclohexyltoluene) and. DMDCH (dimethyldicyclohexyl) was also detected at high conversion. During hydrotreating of

4,6-DMDBT and quinoline, the main product from quinoline hydrogenation (HYD) was 1,2,3,4-tetrahydroquiniline (1THQ) and 5,6,7,8-tetrahydroquinoline (5THQ) was detected in very small amount. Decahydroquinoline (DHQ) was not detected in this study. Hydrodenitrogenated products, propylcyclohexene (PCHE), proplycyclohexane (PCH) and propylbenzene (PB), were not detected because the concentration of quinoline added was very small and 1THQ and 5THQ were only converted very slowly to hydrodenitrogenated products.

The conversion of 4,6-DMDBT was very low over NiMo and CoMo sulfides catalysts at all reaction conditions when 4,6-DMDBT was hydrotreated in the presence of quinoline. It was under 6% after reaction of 47 minutes although the amount of quinoline added was very low, 150ppm N (0.15 wt % quinoline). At the beginning of reaction of 4,6-DMDBT and quinoline with hydrogen, the reaction rate of 4,6-DMDBT was very slow while that of quinoline was very fast. The conversion of quinoline was over 85% just 2 min after starting the reaction and most of the quinoline was converted after reaction time of 7 min.

In general, HDS of individual sulfur compound follows the pseudo-first-order kinetics, thus:

$$\ln(C_{DMDBT}/C_{DMDBT0}) \;=\; -(k_1 + k_2) \cdot t \qquad\qquad (1)$$

where k_1 is the pseudo first-order rate constant for the hydrogenation pathway, and k_2 is the pseudo first-order rate constant for the hydrogenolysis pathway. The value of (k_1+k_2), the overall rate constant, can be calculated from experimental data. **Figure 6** shows the

pseudo first order kinetic profiles of 4,6-DMDBT HDS in the presence of and in the absence of quinoline over CoMo and NiMo sulfide catalysts. The overall rate constants calculated on the basis of the experimental data are shown in **Table 7.** The overall rate constants over NiMo and CoMo sulfides were very low, 5.03×10^{-5} $s^{-1}g \cdot cat^{-1}$ and 3.39×10^{-5} $s^{-1}g \cdot cat^{-1}$, respectively.

In this study, the individual rate constants for each reaction pathway were calculated by using the method suggested in our previous work [9]. In this method, the ratio of k_1/k_2 was calculated by the ratio of the initial selectivity of primary products, as shown below:

$$\frac{k_1}{k_2} = \frac{\left[\text{Initial Selectivity of HDMDBT}\right]}{\left[\text{Initial Selectivity of DMBP}\right]} \qquad (2)$$

Table lists the calculated rate constants for each reaction pathway with and without the presence of nitrogen compound (quinoline).

As shown in **Table 7**, the nitrogen compound quinoline is a very strong inhibitor on 4,6-DMDBT HDS. 4,6-DMDBT hardly converted to HDMDBT or DMBP in the presence of quinoline. After quinoline was converted to 1THQ which was main product from quinoline hydrogenation, the reaction rate of 4,6-DMDBT is still slow. This is because 1THQ is also a basic nitrogen compound which is a strong inhibitor to HDS reaction on the catalysts [38,39].

As shown in **Table 7,** quinoline significantly inhibited both reaction pathways over NiMo and CoMo sulfide catalyst. The loss of hydrodesulfurization activity was over 90% for hydrogenation pathway and hydrogenolysis pathway. Therefore, deep hydrodesulfurization needs more nitrogen tolerant catalysts than traditional NiMo and CoMo sulfide catalysts.
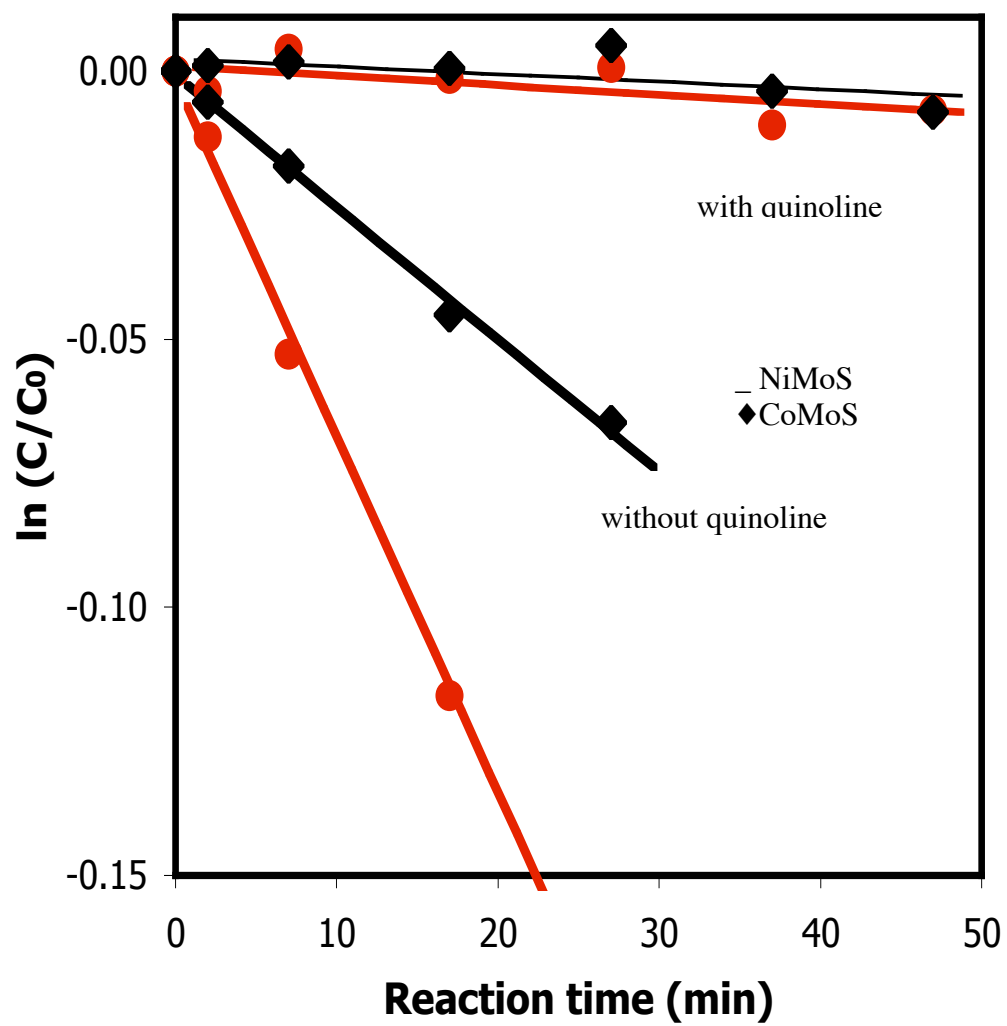
Figure 6. The effect of quinoline on hydrodesulfurization of 4,6-DMDBT over NiMo sulfide and Ni phosphide.

Table 7. Kinetic Results for the Effect of Nitrogen Compounds on Hydrodesulfurization of 4,6-DMDBT

Inhibitor		Rate constant $(10^{-5}\ s^{-1}\ g \cdot cat^{-1})$	
		Without N	Quinoline
NiMo Sulfide	k_1+k_2	117.21	5.03 (95.7%)[2]
	k_1/k_2[1]	5.36	5.06
	k_1	98.77	4.12 (95.8%)
	k_2	18.44	0.91 (95.0%)
CoMo Sulfide	k_1+k_2	44.15	3.39 (92.3%)
	k_1/k_2[1]	2.26	1.74
	k_1	30.60	2.16 (93.0%)
	k_2	13.55	1.24 (90.9 %)

[1] k_1/k_2 = [Initial selectivity of HDMDBT]/[Initial selectivity of DMBP]
[2] The data in parenthesis indicate the percentage loss of HDS activity after adding 150 ppmw N as quinoline.

3.1.2.2 NiMo supported on mesoporous support MCM-41

The prepared NiMo/MCM-41 catalyst contains around 40 wt% MoO_3 and 11 wt% NiO, which are very high metal amount as compared with traditional commercial CoMo and NiMo catalysts. The MCM 41 support, which was prepared with SiO_2/Al_2O_3 ratio of 50 in our laboratory, has surface area of 1113 m^2/g and pore volume of 1.33 ml/g, which is much higher than those of Al_2O_3. So, we loaded a higher amount of Ni and Mo metals on the MCM-41 supports. **Table 8** shows the overall and individual rate constant for each reaction pathway over NiMo catalysts in 4,6-DMDBT HDS. The overall rate constant over NiMo/MCM-41 was 40.18×10^{-5} $s^{-1}g \cdot cat^{-1}$ and was higher than those over NiMo/Al_2O_3 catalysts, which were 36.46×10^{-5} $s^{-1}g \cdot cat^{-1}$ on low metal loaded NiMo/Al_2O_3 and 37.07×10^{-5} $s^{-1}g \cdot cat^{-1}$ on high metal loaded NiMo/Al_2O_3. In the case of alumina supported catalysts, low metal loaded catalyst, which contains 14.0 wt% MoO_3 and 3.0 wt% NiO, has very similar overall rate constant to high metal loaded catalyst, which

contains as the same metal amounts as NiMo/MCM-41. Therefore, the low metal loading is the optimum metal amount on alumina-supported catalyst as reported by many researchers. However, the high metal loaded NiMo/Al$_2$O$_3$ had higher k_1/k_2 ratio than the low metal loaded one. It may be because stacked NiMoS layer produce more active sites for DDS reaction pathway, but the effect was not much.

Table 8. Rate constants of 4,6-DMDBT HDS over sulfided NiMo catalysts supported MCM-41 or Al_2O_3

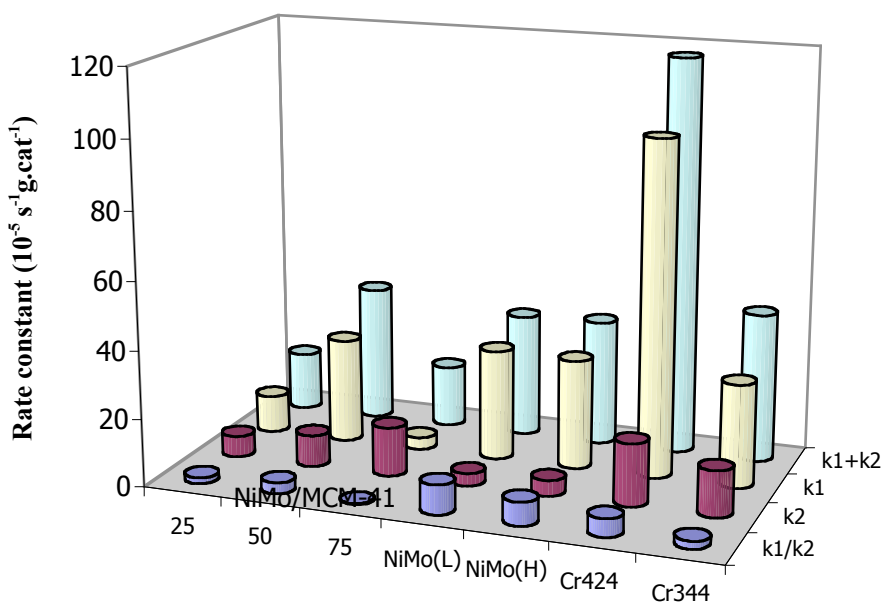| Rate constant (10^{-5} s^{-1} g·cat^{-1})	NiMo/MCM-41 ($SiO_2/Al_2O_3 = 50$)	NiMo/Al_2O_3 (Low)	NiMo/Al_2O_3 (High)	Cr424	Cr344
k_1+k^2	40.18	36.46	37.07	117.21	44.15
k_1/k_2	3.30	8.74	6.90	5.36	2.26
k_1	30.84	32.72	32.38	98.77	30.61
k_2	9.34	3.74	4.69	18.44	13.55
NiO wt%	11.00	3.00	11.00	3.00	3.00
MoO_3 wt%	40.00	14.00	40.00	14.00	14.00

Figure 7. The comparison of the HDS rate constants over NiMo catalysts.

The NiMo/MCM-41 is more active on 4,6-DMDBT HDS than NiMo/Al_2O_3 catalysts, but still not better than commercial CoMo and NiMo catalysts. When the

MCM-41 supported NiMo catalyst was prepared with two step method, the surface area of MCM-41 reduced significantly after the calcination of Mo/MCM-41, which was prepared at first step. MCM-41 needs to be treated carefully when it is used with aqueous solutions because its uniform pore structure may be destroyed even at low temperature (around 100 °C) due to water sensitivity [40]. Therefore, it is necessary to improve a metal impregnation method or this mesoporous support to be stable at high temperature.

3.1.3. Summary

Nitrogen compound, quinoline was a very strong inhibitor on 4,6-DMDBT HDS and 1THQ, which was main product from quinoline hydrogenation, was also strong inhibitor. The reaction rate of 4,6-DMDBT was still slow when quinoline was converted to 1THQ over 85%. This is because 1THQ is also a basic nitrogen compound which is a strong inhibitor to HDS reaction on the catalysts. In kinetic study, quinoline significantly inhibited both reaction pathways over NiMo and CoMo sulfide catalyst. The loss of hydrodesulfurization activity was significantly for HYD pathway and DDS pathway. Therefore, deep hydrodesulfurization needs more nitrogen tolerance catalysts than traditional NiMo and CoMo sulfide catalysts.

The NiMo catalyst, which was prepared on mesoporous support, MCM-41, was more active on 4,6-DMDBT HDS than NiMo/Al$_2$O$_3$ catalysts, but still not better than commercial CoMo and NiMo catalysts. The surface area of MCM-41 reduced significantly after the calcination of Mo/MCM-41, which was prepared at first step. Therefore, it is necessary to improve a metal impregnation method to avoid pore destruction or this mesoporous support to be stable at high temperature.

3.1.4. Future work

3.1.4.1 Development of Deep Hydrodesulfurization Catalysts

1. Improving preparation method (changing the two-step impregnation to one-step co-impregnation) to load Co (or Ni) and Mo simultaneously onto MCM-41 support which needs to be treated with water at low temperature and

2. Preparing new type of catalysts (phosphide) and performing hydrodesulfurization and hydrodenitrogenation simultaneously over them; phosphide catalysts is a promising new type catalyst and noble metal sulfides, which will be prepared with different precursors and modified with transition metal HDS catalysts, could be good catalysts for deep hydrodesulfurization.

3.1.4.2 Adsorptive Denitrogenation of Model Feed for Deep Hydrodesulfurization

Adsorptive denitrogenation is to use an adsorbent that could remove most of the nitrogen compounds by adsorption at ambient temperature without using any hydrogen, followed by hydrodesulfurization of the pre-treated feedstock. This is a promising approach since trace amounts of nitrogen could affect deep desulfurization. Adsorption removal of nitrogen and sulfur will also be examined.

Subtask 3.2. Saturation of Two-Ring Aromatics

As a part of the DOE refinery integration project, this sub-task aims at saturating aromatics for high-quality diesel and jet fuels. High aromatics content in distillate fuels is undesirable since it lowers the fuel quality and contributes to the formation of

environmentaly harmful emissions [41, 42]. In general, lower aromatics content leads to increased thermal stability, improved combustion characteristics and less soot formation. The conventional method of dearomatization is by aromatics saturation (hydrogenation) [41]. Typically, sulfided Co-Mo/Al$_2$O$_3$ or Ni-Mo/Al$_2$O$_3$ catalysts are employed for hydrogenation. However, these catalysts are most active at higher temperatures where equilibrium limitations may prevent complete hydrogenation. Noble-metal catalysts are active at lower temperatures, where equilibrium limitations can be overcome, however sulfur-tolerance is a major obstacle to their commercial application.

To meet the fuel performance and compositional specifications for diesel fuel, it is necessary for both RCO and LCO to be hydrogenated [43, 44]. This work focuses on the development of increasingly sulfur-tolerant, noble-metal catalysts for the low-temperature hydrotreating and dearomatization (LTHDA) of distillate fuels for the production of ultra-clean and low-aromatic diesel fuels. The objectives of this work are to examine the effects of the structure of catalyst support and the influence of metal species and bimetallic combinations on low-temperature dearomatization.

3.2.1 Experimental

3.2.1.1 Catalyst Preparation

In order to examine the effects of support type and structure of pore channels, a series of catalysts was prepared using Palladium as the metal on various supports. Support types used included Y zeolite, mordenite, HZSM-5, alumina, titania, silica-alumina, and the mesoporous alumnosilicate of MCM-41 type. Each catalyst was

prepared using the incipient wetness impregnation (IWI) technique, with $PdCl_2$ as the metal precursor. A summary of all catalysts prepared is found in **Table 9.**

Table 9 Summary of the physical properties and preparation conditions of the catalyst.

Catalyst	Metal Loading	Support Type	Support Code	Bulk Density (g/mL)	Support Surface Area (m^2/g)	SiO_2/Al_2O_3 Ratio	Metal Precursor
Pd/HY(5)	2.0	Y Zeolite	Aldrich 33,441-3	0.50	920	5.4	$PdCl_2$
Pd/HY(30)	2.0	Y Zeolite	CBV720	0.32	780	30	$PdCl_2$
Pd/HY(80)	2.0	Y Zeolite	CBV780	0.34	780	80	$PdCl_2$
Pd/HM(38)	2.0	Mordenite	CBV30A	0.41	512	38	$PdCl_2$
Pd/HM(90)	2.0	Mordenite	CBV90A	0.41	500	90	$PdCl_2$
Pd/HM(20)	2.0	Mordenite	CBV21A	0.41	500	20	$PdCl_2$
Pd/HZSM-5(80)	2.0	ZSM-5	CBV8014	0.44	425	80	$PdCl_2$
Pd/Al$_2$O$_3$	2.0	Alumina	UOP	0.52	170	-	$PdCl_2$
Pd/SiO$_2$-Al$_2$O$_3$	2.0	Silica-Alumina	Aldrich 34,335-8	0.41	475	7	$PdCl_2$
Pd/TiO$_2$	2.0	Titania	Degussa P25	0.78	71	-	$PdCl_2$
Pd/MCM-41(50)	2.0	Al-MCM-41(50)	MCM-41(50)	0.40	1289	50	$PdCl_2$

3.2.1.2 Experimental

A fixed-bed, flow reactor has been designed and constructed to carry out low-temperature dearomatization experiments. It was determined that tetralin (1,2,3,4-tetrahydronaphthalene) be used as a model aromatic compound in this study because it has been shown that saturation of the second aromatic ring is more difficult and rate-limiting in the total hydrogenation process. As a model compound for diesel fuel, hexadecane (cetane) is used as a carrier for the feedstock. Nonane is added as an internal standard for GC/MS analysis. Feedstock composition for the dearomatization experiements is 20 wt% tetralin, 75 wt% hexadecane and 5 wt% nonane, with ppm quantities of sulfur, as benzothiophene (BT), added for certain experiments.

For each experiment, 0.5g of catalyst was used. To this is added 3.0g of α-alumina as a diluent, and the catalyst/diluent is packed in the reactor. Prior to each experiment, catalysts are reduced in-situ under a flow of 100 mL/min hydrogen. The pressure is maintained at 100 psi. The temperature program is as follows: Beginning at room temperature, the temperature is increased at a rate of 2°C/min until the temperature reaches 225°C. The temperature is then maintained at 225°C for 2 hours before the pressure is increased to the reaction pressure of 600 psi. When the reaction pressure is reached, the hydrogen flowrate is decreased to 80 mL/min and the liquid feed is started. The liquid flowrate is 0.08 mL/min. This corresponds to a WHSV of approximately 8hr^{-1} and a gas-to-liquid ratio of approximately 1000. Reaction and reduction conditions are summarized in **Table 10**.

Initially, the liquid feed contains no sulfur. The sulfur-free feed is allowed to equilibrate for 90 min before the first sample is taken. Thereafter, samples are taken every 30 minutes. After 150 minutes of sulfur-free feed, the feedstock is switched to one which contains sulfur. For the initial set of dearomatization experiments, the concentration of sulfur was 37 ppm sulfur as benzothiophene (BT).

Table 10: Reduction and Reaction Conditions

	Reduction	Reaction
Temperature:	25°C - 2°C/min - 225°C - 120 min @ 225°C	225°C
Pressure:	100 psi	600 psi
Hydrogen Flowrate:	100 mL/min	80 mL/min
Liquid Flowrate:	-	0.08 mL/min
WHSV:	-	~8 hr^{-1}
G/L:	-	1000

3.2.2 Results and Discussion

The results of the initial dearomatization experiments are shown in **Figure 8**. It can be seen that even after 300 minutes time-on-stream (TOS) after the introduction of 37

ppm sulfur feedstock, nearly all of the catalysts tested maintained 100% conversion of tetralin to decalins. Unfortunately, this means that not much distinction can be made amongst any of the catalysts. For this reason, it was decided that the concentration of sulfur be increased to 100 ppm while maintaining all other reaction parameters the same. Preliminary indications for these new experimental conditions are promising. **Figure 9** shows the results of the first three experiments with 100 ppm sulfur feedstock. Differences in activity can clearly be seen using the 100 ppm feedstock. Palladium supported on Y zeolite with a SiO_2/Al_2O_3 ratio of 80 shows much higher sulfur tolerance than Pd/Al_2O_3 or Pd/HM(90).

Conversion vs. TOS
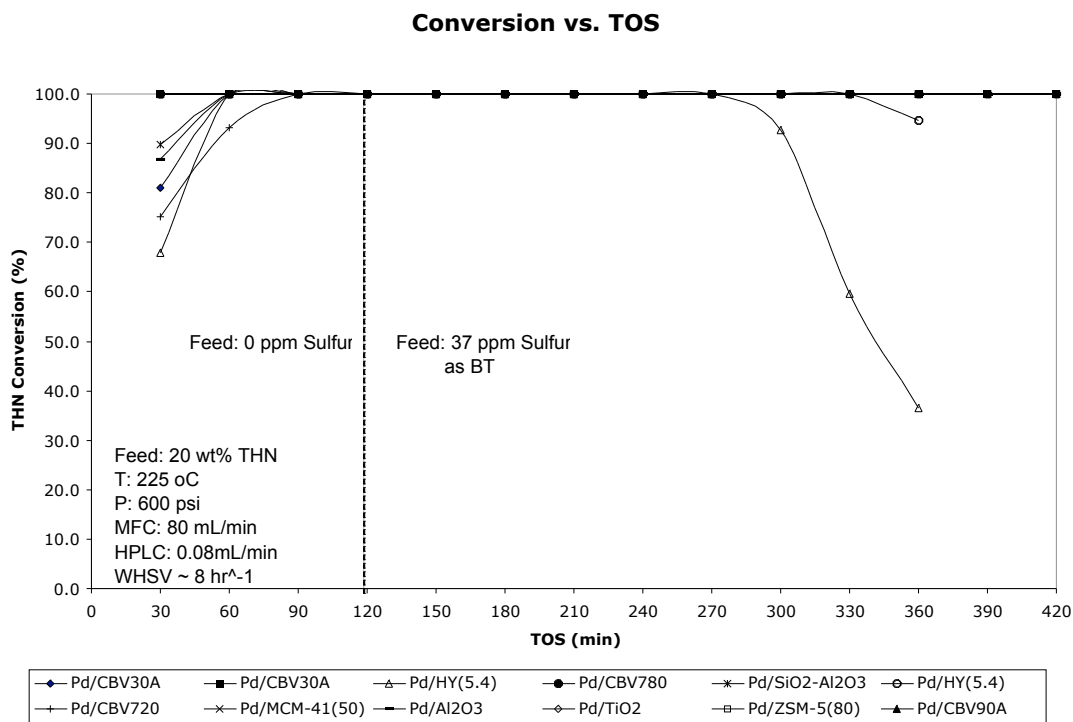
Figure 8 Results for initial dearomatization experiments
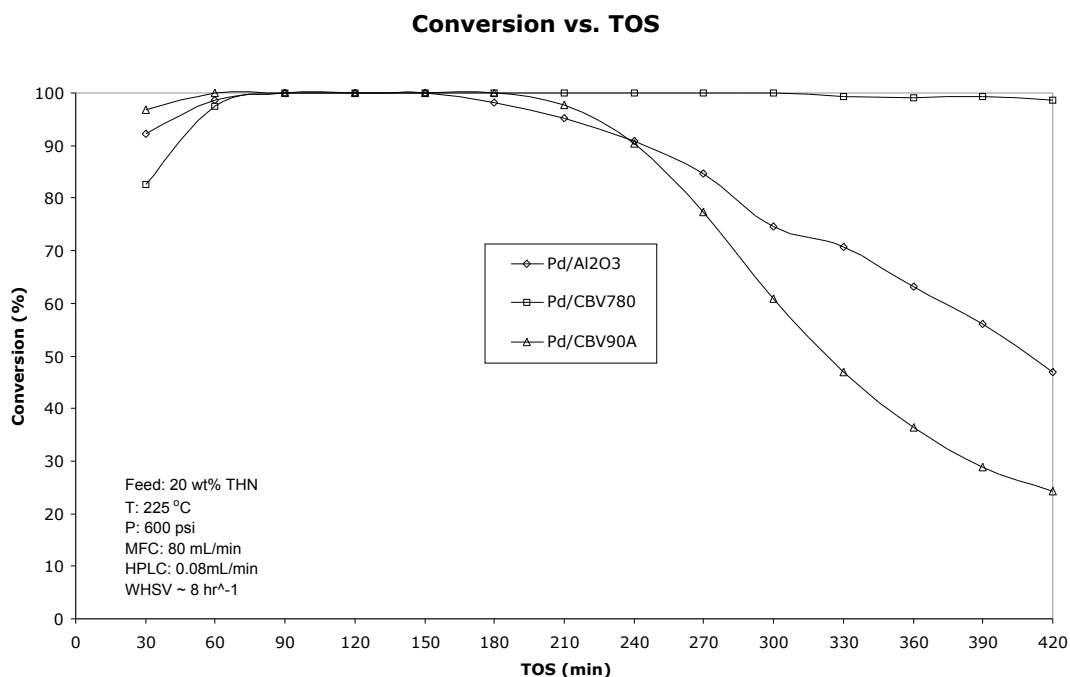
45

Conversion vs. TOS

Figure 9. Results for dearomatization experiments with 100 ppm sulfur feedstock

3.2.3 Summary

A fixed-bed flow reactor was designed and constructed to carry out dearomatization experiments. A series of catalysts were prepared using Palladium as the active metal on various supports, including Y zeolite, mordenite and mesoporous aluminosilicate MCM-41, for the purposes of examining the effect of support type and structure of support pore channels. Dearomatization experiments were conducted using the catalysts prepared. The initial experiments were conducted at a temperature of 225°C under a hydrogen pressure of 600 psi. The WHSV was approximately 8 hr^{-1} and the hydrogen to liquid ratio was approximately 1000. The feedstock contained 37 ppm sulfur (as benzothiophene). The results of this initial series of experiments did not allow for much differentiation between the various catalysts, as all catalysts maintained high

activity for the duration of the experiment. It was determined that the amount of sulfur in the feedstock should be increased to 100 ppm, and preliminary results from experiments conducted using this feedstock yielded results which allow for better examination of the support effects.

3.2.4   Future Work

After the series of catalysts are tested to examine the support effect, new catalysts will be synthesized and tested using Pt, Ru and Ni in addition to Pd and bimetallic catalysts with combinations of these metals will also be prepared and tested. Commercial hydrogenation catalysts will also be obtained and tested for comparison. Once the effects of all factors studied have been determined and the most promising catalysts have been identified, desulfurized and denitrogenated RCO and LCO will be used as the feedstock for dearomatization.

Subtask 3.3. Value-Added Chemicals from Naphthalene and Biphenyl

It is important to point out that refinery produces not only fuels, but also chemical feedstock for the chemical process industry that generate useful products such as plastics, fibers, and rubbers. While the bulk of RCO and LCO can be processed to make advanced thermally stable jet fuels, a part of the aromatics can be used for making value-added aromatic chemicals. Recent studies [45, 46] indicate that high-value chemicals can be obtained by selective conversion of polycyclic hydrocarbons such as naphthalene, biphenyl, and phenanthrene, over some zeolite catalysts. The products of such selective

reactions are specialty chemicals, monomers of advanced polymer materials such as high-performance polyesters, advanced engineering plastics, and liquid crystalline polymers.

Chemical analyses of RCO and LCO clearly indicate that naphthalene is the representative structure of aromatics in these fractions, and at least over 60 % of RCO and LCO are aromatic components that have the naphthalene structure. Because 2,6-dialkylnaphtahlene is the intermediate of monomer for making engineering plastics such as polyethylene naphthalate, polybutylene naphthalate and liquid crystalline, selective alkylation of naphthalene to 2,6-dialkylnaphtahlene is a highly value-added reaction. However, most literature studies deal with isopropylation. But methylation is more desirable for industrial applications although methylation is more difficult [47]. To realize the shape-selective methylation of naphthalene to produce 2,6-dimethylnaphthalene (2,6-DMN), shape-selective zeolite catalyst for selective reaction of naphthalene with methanol inside the channel was proposed. In this report period, a fixed bed flow reaction system for the methylation of naphthalene to produce 2,6-DMN was set up. Preliminary experiment on the effect of types of zeolites and $SiO_2/Al2O_3$ ratio of zeolites on the methylation of 2-methylnaphthalene (2-MN) were investigated.

3.3.1. Experimental

3.3.1.1 Catalysts

Three types of zeolites, i.e., HY, H-Mordenite (HM) and HZSM-5, were used as catalysts. The $SiO_2/Al2O_3$ ratio of HY, H-Mordenite and HZSM-5 are 80, 90 and 80, respectively. HZSM-5 with different the $SiO_2/Al2O_3$ ratio of 50, 80 and 280, respectively, were also tested. All the zeolite samples were obtained from Zeolyst

International. Details on the physical properties of the catalyst are listed in **Table 11**. Zeolites with ammonium form were calcined at 450 $^\circ$C for 6 hours to convert to hydrogen form.

3.3.1.2 Catalyst Evaluation

Catalytic testing was carried out in a down-flow fixed bed reactor system as shown in **Figure 10**. In a typical run, 0.3 gram catalyst (10-18 mesh) loaded in reactor tube (Pyrex, I.D.: _ inch) was placed in the furnace center. The catalyst was activated at 450 $^\circ$C for 1 h under the inert N_2 gas flow (20 ml/min). Then the temperature was cooled down to the reaction temperature of 300 $^\circ$C. Reactant dissolved in mesitylene solvent (2-methylnaphalene:methanol:mesitylene=1:5:5 mol ratio) was fed into reactor through a HPLC pump at the flow rate of 1.98 ml/min together with 20 ml/min carrier N_2 gas flow. The reaction product was collected at 1 hour interval. Both the reactants and products were analyzed by HP 5890 gas chromatography (GC) with a β-Dex 120 capillary column (60m, 0.25 mm I.D. column with 0.25 micrometer coating film thickness). The ratio of 2,6-DMN/2,7-DMN will be determined and used as a key parameter to evaluate catalyst selectivity feature.

Table 11 Physical properties of the catalysts

Catalyst Type	Support Code	Na$_2$O (wt%)	Surface Area (m^2/g)	SiO$_2$/Al$_2$O$_3$ Ratio
HY	CBV780	0.03	780	80
HM	CBV90A	0.05	500	90
NH$_4$ZSM-5	CBV8014	0.05	425	80
NH$_4$ZSM-5	CBV5524G	0.05	425	50
NH$_4$ZSM-5	CBV28014	0.05	400	280

Figure 10 Picture of the flow reaction system.

3.3.2 Results and Discussion

3.3.2.1 Types of zeolites on the methylation of 2-MN

Various large-pore (HY and HM) zeolite and medium-pore (HZSM-5) were tested for the methylation of 2-MN. The changes in 2-MN conversion, 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio with time on stream are shown in Figures 11. The initial reactivity of the catalysts decreases in the following order: HM>HY>HZSM-5. However, HY and HM deactivates faster than HZSM-5. HZSM-5 also shows a higher 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio than HY and HM. Low 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio of HY and H-M is believed to be caused by the large poreport of these zeolites, which easily accommodate many competitive reaction product molecules, e.g., DMN isomers, ethylnaphthalene (EN) and trimethyl naphthalene,
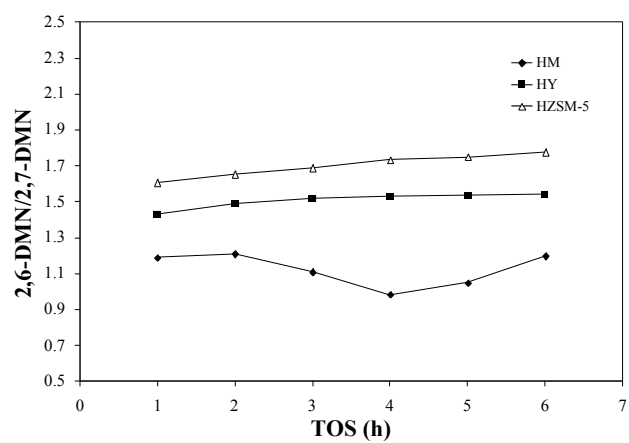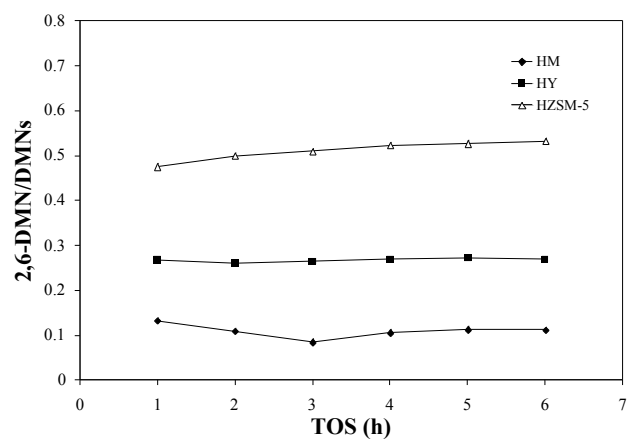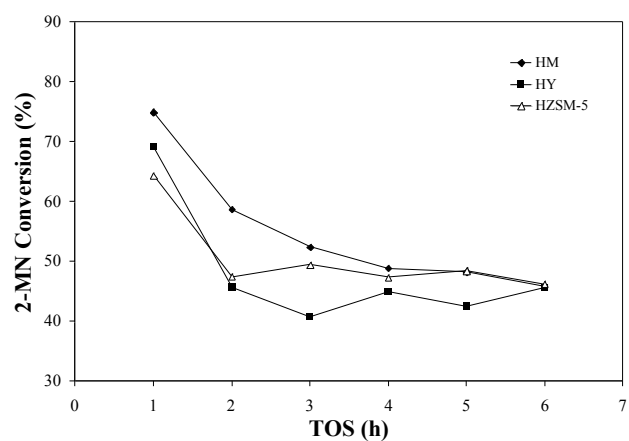
Figure 11 Effect of catalyst type in methylation of 2-MN with methanol. Reaction condition: temperature: 300 $^{\circ}$C; Feed (2-MN:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min

etc, and allow their rapid diffusion. Similar trend was reported in the literatures [48, 49]. Therefore, HZSM-5 shows a better catalytic effect on the methylation of 2-MN than the HY and HM.

3.3.2.2 SiO$_2$/Al$_2$O$_3$ Ratio of HZSM-5 on the Methylation of 2-MN

Besides the pore size, acidity also plays an important role on the methylation of 2-MN. The acidity of zeolites is generally determined by their SiO$_2$/Al$_2$O$_3$ ratio. The effect of SiO$_2$/Al$_2$O$_3$ ratio of HZSM-5 on the methylation of 2-MN was also investigated. **Figures 12** show the changes in conversion, 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio with time on stream. HZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio of 80 shows the highest and most stable catalytic activity among the HZSM-5 zeolites investigated. When the SiO$_2$/Al$_2$O$_3$ ratio of HZSM-5 is low, the catalyst has a strong acidity and therefore causes the quick coke deposition. The catalyst deactivates faster than that with high SiO$_2$/Al$_2$O$_3$ ratio. When the SiO$_2$/Al$_2$O$_3$ ratio of HZSM-5 is high, the catalyst has a weak acidity. Therefore, the catalytic activity for methylation of 2-MN is lower than that of the catalyst with low SiO$_2$/Al$_2$O$_3$ ratio. 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio show a similar trend. HZSM-5 with medium acidity, i.e., SiO$_2$/Al$_2$O$_3$ ratio of 80, shows the best 2,6-DMN selectivity and highest 2,6-DMN/2,7-DMN ratio among the HZSM-5 zeolites investigated. The 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio increases with time on stream for HZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio of 50 and 80, while the 2,6-DMN selectivity and 2,6-DMN/2,7-DMN ratio decreases with time on stream for HZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio of 280.
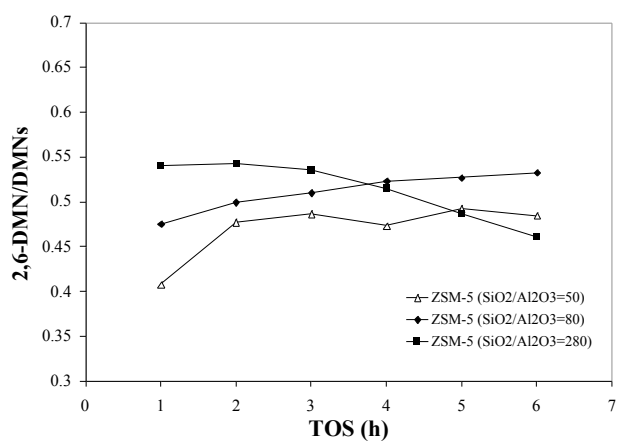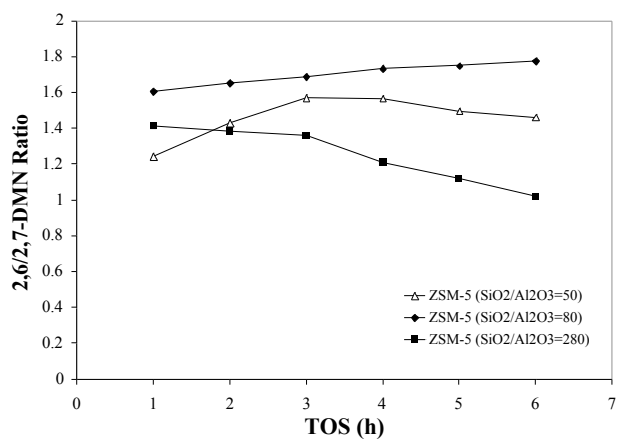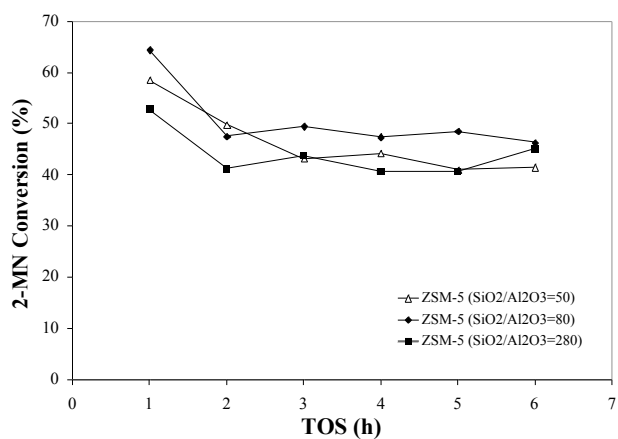
Figure 12 Methylation of 2-MN with methanol over HZSM-5 zeolite with different SiO₂/Al₂O₃ ratio. Reaction conditions: temperature: 300 °C; Feed (2-MN:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min

3.3.3 Summary

1. HZSM-5 zeolite with medium pore size is a better catalyst than the HY or HM zeolite with large pore size for the selective methylation of 2-MN with methanol to produce 2,6-DMN.

2. HZSM-5 with moderate acidity shows the best reaction activity, catalyst stability and 2,6-DMN selectivity.

3.3.4 Future work

Future work will focus on the improvement of the activity, selectivity and stability of the ZSM-5 zeolite and MFI molecular sieve catalysts.

(1)　To modify the ZSM-5 zeolite or MFI molecular sieves with metal or metal oxide to adjust the acidity, confine the pore size and load active catalytic species; Catalyst with the best combination of acidity, pore size and catalyst species will be determined.

(2)　 To prepare ZSM-5 zeolite or MFI molecular sieves with different particle size. Particular attention will be paid to the nanosized ZSM-5 zeolite and MFI molecular sieves;

(3)　To prepare ZSM-5 zeolite or MFI molecular sieves with different crystal shape, i.e., different length of channels, to clarify the function of different channels in ZSM-5 zeolite or MFI molecular sieves on the selective methylation of 2-MN with methanol to produce 2,6-DMN.