A Kinetic Study of the Hydrogenation and Dimerization of Styrene and α -Methylstyrene on

Ni-Mo-S Catalyst

by

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Abstract

Oilsands bitumen upgrading to produce naphtha, among other products, is a feasible approach to increasing the supply of refined oil products. However, naphtha derived from bitumen is relatively unstable as it contains unsaturated hydrocarbons (5 vol% diolefins, 15 wt% aromatics). The unsaturated hydrocarbons tend to polymerize and form carbonaceous deposits on the catalyst during mild hydrotreating (~200 °C), resulting in pressure build-up in the reactor that causes the early shut down of the hydrotreating unit. This dissertation addresses diolefin hydrogenation and dimerization kinetics and gum formation over a commercial Ni-Mo-S hydrotreating catalyst. Two model compounds, styrene and α -methylstyrene (AMS), were selected to represent the diolefin present in the naphtha feed. Styrene reactions were based on orthogonal analysis with temperature (200, 225, 250 °C), diolefin concentration (3.7-7.4 wt%), and catalyst amount (0.5, 1, 2 g) varied. For the AMS reactions, a single variable test was applied by changing the AMS content (4.2-6.3 wt%) or temperature (200, 225 and 250 °C). The styrene and AMS hydrogenation kinetics were developed as 1st-order in reactant and 0-order in H₂, based on a simplified Langmuir-Hinshelwood (L-H) model. Pseudo 1st-order in model compound kinetics was employed for the dimerization reaction. The results revealed that the rate of hydrogenating or dimerizing styrene was faster than AMS due to steric hindrance effects. The activation energy for styrene and AMS hydrogenation was 45.3 and 87.7 kJ/mol, respectively. The activation energy for styrene dimerization was 99.6

kJ/mol. Additionally, the relationship between dimer content and gum formation at the end of the reaction indicated that higher dimer concentration increased gum content in styrene reactions. However, this relationship was not observed in AMS reactions because of steric hindrance effects.

Finally, competitive reactions between olefins and diolefins were also examined. Cyclohexene hydrogenation to cyclohexane was initially suppressed by AMS hydrogenation to cumene. With longer reaction time (510 mins), the cyclohexane concentration exceeded cumene, suggesting that competitive hydrogenation occurred between the cyclohexene and AMS. Adding cyclohexene to the AMS significantly reduced the dimer content in the product possibly due to competitive adsorption on the acidic sites.

Preface

All of the experimental work and thesis were finished in the Department of Chemical and Biological Engineering at the University of British Columbia.

I, Xu Zhao, was the major researcher of this project, responsible for all major areas of experimental operations, data collection and analysis, as well as the dissertation formation. Kevin J. Smith was the supervisor of this project, involved throughout the research design and dissertation edits. The autoclave reactor described in experimental section 2.1 was built by Ali Alzaid to conduct all my experiments and collect liquid samples during reaction. Figures 2-6 were used with permission from APS physics (copyright, 2000) and Elsevier (copyright, 2007 and 2001). Portion of the coke formation as presented in section 1.2.3 was modified from Bartholomew's book (Fundamentals of Industrial Catalytic Process).

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Nomenclature

Roman symbols

a	external surface area of catalyst particles, m ⁻¹
А	Styrene
A _{area}	GC-MS area, dimensionless
В	Decalin
C _{A0}	Initial styrene or AMS concentration, mol/cm ³
C _D	Dimer concentration, mol/cm ³
C _{D0}	Initial styrene or AMS dimer concentration, mol/cm ³
C _{H2}	Dissolved H ₂ concentration, mol/cm ³
$C_{H \cdot S_v}, C_{R \cdot S_v}, C_{RH \cdot S_v}$	Adsorbed H ₂ , styrene or AMS, and intermediates, respectively, mol/gcat
C _R	Styrene or AMS concentration, mol/cm ³
C _{R2H}	Ethylbenzene or cumene concentration, mol/cm ³
C _t	Total available sites, mol/gcat
C _{th}	Thiophene concentration, mol/cm ³
d_{fl}	Degrees of freedom between groups
d _{f2}	Degrees of freedom within groups

d _p	Catalyst particle diameter, m
d _{ST}	Stirrer diameter, m
D _{AB}	Diffusivity of A in B, m ² /s
D _e	Effective diffusivity, m ² /s
D _{H2}	H_2 diffusivity in decalin, m ² /s
E _a	Activation energy, kJ/mol
f	Tested variable of orthogonal analysis
F	ANOVA F values, dimensionless
g	Gravity constant, m/s ²
G	Gum content, mg/100mL
k	Group numbers for ANOVA analysis
k ₀	pre-exponential factor, cm ³ ·min ⁻¹ ·g ⁻¹
k _c a	external mass transfer coefficient, s ⁻¹
$sh = \frac{k_c d_p}{D_{AB}}$	Sherwood number, dimensionless
k _{Dimer}	Dimerization rate constant, cm ³ ·min ⁻¹ ·g ⁻¹
k _{HYD}	Hydrogenation rate constant, cm ³ ·min ⁻¹ ·g ⁻¹
k _L a	Gas-liquid mass transfer coefficient, s ⁻¹
K4 K2 K2	Adsorption equilibrium constants of H ₂ , Styrene or AMS, and intermediates,
••1,••2,••3	respectively, cm ³ /mol

K _{th}	Adsorption equilibrium constants of thiophene, cm ³ /mol
m	catalyst loading, kg/m ³
m/z	Mass-to-charge, kg/Coulombs
m _b	Beaker mass difference before and after analysis, g
m _s	Residue mass difference before and after analysis, g
M _B	Decalin molecular weight, kg/mol
MI	Mixing speed, rpm
MSA	Mean square values between groups
MSE	Mean square values within groups
n	Data sets for ANOVA analysis
N _{pe}	Peclet number, dimensionless
N _T	Stirrer speed, s ⁻¹
P _{H2}	Hydrogen pressure, MPa
PI	Reaction pressure, Psi
r _{HYD}	Hydrogenation rate, $mol \cdot min^{-1} \cdot g^{-1}$
R	Gas constant, 8.314 J·K ⁻¹ ·mol ⁻¹
R ²	Degree of explanation
S _v	Vacant sites, mol/gcat
SSA	Sum of squares between groups

SSE	Sum of squares within groups
SST	Total sum of squares between groups
t	Reaction time, min
Т	Reaction temperature, K
$\overline{T_1}$	Average experimental values of orthogonal analysis for ANOVA analysis
TI1	Reaction temperature signal, °C
TI2	Heating jacket temperature signal, °C
TT	Thermocouple
u _{Ea}	AMS dimerization activation energy uncertainty, kJ/mol
$\tilde{\mathrm{V}}_{\mathrm{A}}$	Styrene molar volume, m3/mol
X	Conversion
x _i	Experimental values
x	Averaged experimental values
$\overline{\overline{\mathbf{X}}}$	Averaged both experimental and calculated values for ANOVA analysis
X1j	Experimental values for ANOVA analysis
X2j	Calculated values for ANOVA analysis
X _{oo}	Experimental values of orthogonal analysis for ANOVA analysis
Z	Number of repeat experiments

Greek symbols

α	Single factor
γ	Decalin surface tension, N/m
η	Effectiveness factor, dimensionless
μ	Decalin viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
ρ	Decalin density, kg/m ³
Δρ	Density difference between particle and solution (decalin), $\rho_p - \rho$, kg/m ³
$ ho_b$	Bed density, g/cm ³
ρ_p	Catalyst particle density, kg/m ³
σ _c	Constriction factor, 0.8, dimensionless
ĩ	Tortuosity, 3.0, dimensionless
ϕ_B	Association parameter, 1 for decalin, dimensionless
ϕ_p	Pellet porosity, 0.4, dimensionless
Ø1	Thiele modulus for the 1 st -order reaction, dimensionless

Acronyms and abbreviations

AMS α-methylstyrene

ANOVA	Analysis of variance
ASA	Amorphous silica alumina
ASTM	American Society for Testing and Materials
bp	Boiling point, °C
BET	Brunauer-Emmett-Teller
BP	British Petroleum
С	Concentration, mol/cm ³
cat	Catalyst
cus	Coordinatively unsaturated
CW	Cooling water
GC	Gas chromatography
G-L	Gas-liquid
GC-MS	Gas chromatography-mass spectrometry
HDS	Hydrodesulfurization
HGO	Heavy gas oil
L-H	Langmuir-Hinshelwood
LGO	Light gas oil
MS	Mass spectrometry
MSD	Mass spectrometry detector

MW	Molecular weight, g/mol
N	Nitrogen
NIST	National Institute of Standards and Technology
PE	Perkin Elmer
РТ	Pressure transducer
PYGAS	Pyrolysis gasoline
Re	Reynold's number, dimensionless
RF	Response factor
RPM	Revolutions per minute
RSD	Relative standard deviation
S	Sulfur
Sc	Schmidt number, dimensionless
SD	Standard deviation
STM	Scanning tunneling microscopy
TIC	Total ion chromatogram
UOP	Universal Oil Product
We	Weber number, dimensionless

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and

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Chapter 1. Introduction

1.1 Background

As oil consumption has dramatically increased worldwide over the past several decades, it is indisputable that the oil demand is far outweighed by the oil supply, despite recent oversupply issues. According to the BP statistical review of world energy published in June, 2015 [1], world oil production was 8.87 million barrels per day in 2014, whereas daily consumption was 9.21 million barrels. Although the difference between the production and consumption accounts for stock variation, consumption of substitute fuels and different data sources, the large demand for crude oil has meant that there is a renewed interest in developing the Canadian oilsands to meet the market need. The oilsands deposits of Alberta, Canada are equivalent to approximately 168 billion barrels of crude oil, making them the third largest crude oil reserves in the world [2]. Oilsands contain approximately 10 wt% bitumen (Fig. 1). After removal of the associated water and sand, the bitumen is upgraded by coking or hydroconversion processes.



Figure 1. A schematic showing the composition of oilsands deposits. Adapted from Alberta Energy website [2].

Coking is a thermal process that requires heating the bitumen to >500 °C, to produce liquid naphtha (boiling point, bp: <177 °C), kerosene (bp: 165-282 °C), light gas oil (LGO, bp: 215-337 °C), and heavy gas oil (HGO, bp: 343+ °C) [3, 4]. These bitumen derived products, following hydrotreatment, can further supply the world demand for refined fuels. A typical example of the composition of the upgraded Athabasca oildsands bitumen from Syncrude is shown in Table 1 [4].

Coker products	Naphtha	LGO	HGO
Composition, vol%	34.1	16.4	49.5
Sulfur, wt%	1.68	3.64	4.33
Nitrogen, ppm (wt)	237	1,600	3,780

Table 1. Typical coker liquid product composition from Athabasca oildsands bitumen [4].

One major concern regarding the products generated from bitumen upgrading by coking is that the naphtha produced is unstable and contains a significant amount of unsaturated hydrocarbons in the form of olefins (30 vol%), diolefins (5 vol%) [4], and aromatics (15 wt%) [5]. These unsaturated hydrocarbons are highly reactive and may undergo undesired dimerization, polymerization and gum (coke) formation reactions during hydrotreatment. The high molecular weight hydrocarbons that result from these reactions will deposit on the catalyst surface resulting in catalyst deactivation and an increase in pressure drop across the hydrotreating reactor.

While the composition of coker naphtha is very complex and dynamic due to a combination of factors such as the source of coker oils and operating conditions, the unstable characteristics of coker naphtha can be improved by two-stage hydrotreating processes that firstly hydrogenate the unsaturated compounds to stabilize the naphtha, followed by hydrotreating at higher

temperature to remove unwanted S-containing and/or N-containing compounds in a second stage. Although the first reactor is operated at low temperature (~200 °C) to reduce the polymerization reactions, the reactor pressure build-up caused by polymeric carbon deposits may still occur resulting in premature shut-down of the unit. Generally, polymerization of diolefins is considered to be the major cause of the pressure build-up in hydrotreators [6].

In past studies, many researchers have investigated the hydrogenation of diolefins over alumina supported noble metal catalysts, such as Pd [7-14]. However, these catalysts are expensive and are easily poisoned by metals, S and N that are present in coker naphtha. Metal sulfide catalysts such as Ni-Mo-S/Al₂O₃ and Co-Mo-S/Al₂O₃ catalysts also have high activity and selectivity for the hydrogenation of unsaturated hydrocarbons [15], and since they have a much lower cost compared to noble metals (Table 2), they are often preferred, especially if the feed has a significant S content.

Metal	Price (USD/g)
Pd	19.3
Mo ^a	0.021

Table 2. Metal price comparison updated at 11-08-2015 [16].

^a price based on Mo₂O₃.

For example, Syncrude two-stage hydrotreating reactors utilize a commercial Ni-Mo-S/Al₂O₃ catalyst to stabilize the coker naphtha. However, few studies are available that report diolefin hydrogenation, dimerization, and/or polymerization, as well as their kinetics over Ni-Mo sulfide catalysts. Therefore, the goal of the present study is to investigate the kinetics of diolefin hydrogenation and dimerization over a commercial Ni-Mo-S/Al₂O₃ catalyst, at conditions relevant to commercial hydrogenation reactors.

Some nomenclature needs to be defined before proceeding. Polymerization refers to aggregates of thousands of molecules, whereas dimerization is the product of two identical molecules that undergo a coupling reaction. The gum (coke) precursors are assumed to be products of multiple dimerizations. Gum is the residue present in oil after evaporation with steam and solvent washing as per the standard ASTM D381-12 method. When gum undergoes further polymerization reactions (usually at >350 °C), high C/H ratio hydrocarbons are generated that result in coke. In some contexts, the dimerization and polymerization, the gum formation and coke formation are used interchangeably.

1.2 Literature review

1.2.1 Hydrotreating catalysts

Noble metals and metal sulfides supported on Al₂O₃ have been widely studied as hydrotreating catalysts for hydrogenation, hydrodesulfurization (HDS) and hydrodenitrogenation [15, 17-19]. However, considering the higher cost of noble metals (Pd, Ru) compared to metal sulfides (Ni, Mo, Co, W), as well as the presence of S-containing and N-containing compounds in typical hydrotreator feeds that act as poisons of noble metal catalysts [19], they are limited in crude oil refining applications. The relatively low price, and excellent activity and selectivity of metal sulfide catalysts mean that they are preferred and have been widely applied in hydrotreating applications. Co-Mo, Ni-Mo, and Ni-W sulfides are usually chosen for hydrotreating applications because of their longer useable life-time, and their ability to eliminate side reactions that lead to catalyst fouling and pressure build-up in hydrotreators [15]

Wambeke et al. [20] studied the hydrogenation of isoprene with MoS_2/Al_2O_3 (9.2 wt%) at 50 °C and identified that the hydrogenation active sites were the 3 coordinatively unsaturated (cus) Mo ions on the ($\bar{1}010$) edge plane of MoS_2 slabs. In subsequent work [21], by investigating the hydrogenation of cis-1, 3-pentadiene and isoprene at 50 °C over MoS_2/Al_2O_3 (9.2 wt%), Kasztelan et al. further proved that the active sites for hydrogenation

were 3 cus Mo ion in the ($\overline{1}010$) plane and found the active sites for isomerization were 2 or 4 cus Mo ions existing in the same plane. With the development of scanning tunneling microscopy (STM), the first real portrait of the active sites on MoS₂ slabs was obtained as shown in Figure 2 [22].



Figure 2. Left hand side: Atom-resolved STM image of MoS₂ structure on Au (111). White circles are the cus Mo ions. Right hand side: ball model for MoS₂ structure (1010) edge with 100% S coverage (yellow: S, blue: Mo). Reprinted with permission from APS physics, Copyright (2000). [22]

For promoted metal sulfide catalysts, Co-Mo sulfides are preferred for HDS reactions, whereas Ni-Mo sulfides are more suitable catalysts for hydrogenation reactions. NiW catalysts are expensive even though they exhibit the highest hydrogenation ability of aromatics [15]. The active sites for hydrogenation are different on promoted MoS₂ versus MoS₂ catalysts [15].These sites are cus metal atoms associated with the Ni-Mo-S structure, where the location of the promoter (Ni) is related to the Ni-Mo-S particles [23]. For larger particles (61*61 Å², Fig. 3), the Ni is positioned at Ni-Mo-S ($\overline{1010}$) edge whereas the other edge is similar to the unpromoted MoS₂ structure (10 $\overline{10}$) edge.



Figure 3. Left hand side: Atom-resolved STM image of Ni-Mo-S structure (61*61 Å²). Right hand side:
ball model for Ni-Mo-S structure (1010) and (1010) edge (yellow: S, blue: Mo, Cyan: Ni). Reprinted with permission from Elsevier, Copyright (2007). [23]

STM also shows that the Ni atoms are in $(\overline{1}010)$, $(10\overline{1}0)$ and $(11\overline{2}0)$ planes ($(11\overline{2}0)$ edge is an unstable edge, Fig. 4) for smaller Ni-Mo-S particles (39*40 Å²). The promotional

effect is explained that the "loosely" bonded sulfur can be easily "cleaved" and provides several different vacancies to promote catalytic activity [24, 25].



Figure 4. Left hand side: Atom-resolved STM image of Ni-Mo-S structure (39*40 Å²). Right hand side:
ball model for Ni-Mo-S structure (1010), (1010) and (1120) edge (yellow: S, blue: Mo, Cyan: Ni).
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1.2.2 Unsaturated hydrocarbon reaction kinetics

Selective catalytic hydrogenation is one of the most important industrial applications to produce fine chemicals [19], vegetable oils [26] and fuels such as gasoline and diesel [19]. In the context of coker naphtha upgrading, the hydrogenation reaction is conducted with

Ni-Mo-S catalysts in two-stage hydrotreators that firstly remove the unsaturated hydrocarbons under relatively low reaction temperature (~200 °C), followed by a second reactor used for removing the S- and N-containing products.

Few studies have been reported that are related to the topic of hydrogenation of diolefins over metal sulfide catalysts [27, 28]. Okuhara et al. [27] reported that the products of hydrogenating isoprene were 2-methyl-1-butene (77%) and 2-methyl-3-butene (21%) at room temperature with unsupported MoS₂ catalysts. The large difference in component yield was explained by steric hindrance effects caused by varied adsorption abilities of the double bonds. The adsorption of the 3-butene double bond was stronger than that of 1-butene double bond, thus producing more 2-methyl-1-butene. The steric hindrance effect also occurred for the HDS reaction over MoS₂ catalysts [29]. Simpler molecules such as thiols are generally desulfurized more easily than alkyl-substituted hydrocarbons. Hubaut et al. [28] investigated the hydrogenation reactivity of several diolefins and olefins over MoS₂/Al₂O₃ catalysts. Table 3 summarizes the data obtained from Hubaut's work showing that the conjugated diolefins hydrogenated 2-3x's faster than other diolefin structures. These studies have shown that the molecule structure is a key factor that determines the reactivity and product selectivity during hydrotreating reactions.
Reactant	T (0 C)	Hydrogenation activity,	
	Temp (°C)	$10^3 (\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1})$	
Isoprene	50	30	
Penta-1,3-diene	50	35	
Penta-1,4-diene	80	8	
Cyclohexa-1,3-diene	80	14	
2-Methyl-2-butene	150	7	

Table 3. Relative hydrogenation rates of diolefins/olefins over MoS₂/Al₂O₃ catalyst [28].

Much research has focused on the hydrogenation mechanism and kinetics of styrene (conjugated diolefin) as a representative of pyrolysis gasoline (PYGAS) over a wide range of temperatures over Pd catalysts [7, 10, 12, 13]. Cheng et al. [7] studied PYGAS hydrogenation kinetics using styrene and isoprene diluted in toluene as the model compounds. They conducted the experiments in a semi-batch reactor over a range of 60-180 °C, 2.1-4.8 MPa H₂ pressure, with supported Pd catalysts (0.3 wt%). They found that under the reaction conditions, the main styrene hydrogenated product was ethylbenzene and the reverse reaction for styrene hydrogenation could be neglected for simplification. Based on their experimental results, a series of ordinary differential rate equations were proposed to describe the hydrogenation assuming 1st-order kinetics with respect to the reactant. Chaudhari et al. [8]

studied the hydrogenation kinetics for both phenyl acetylene and styrene (ethanol as the solvent) in an autoclave with 0.1 wt% Pd/C catalysts over a temperature range of 15-45 °C under constant H₂ pressure. According to their kinetic results, ethylbenzene was the only hydrogenated product for styrene hydrogenation. Accordingly, they proposed a dual site Langmuir-Hinshelwood (L-H) model to describe the styrene hydrogenation that is 1st-order with respect to H₂ pressure. Both studies concluded that the hydrogenated styrene product ethylbenzene had no significant effects during the reaction. In subsequent work, Zhou et al. [10] investigated both styrene (diluted in n-heptane) and PYGAS hydrogenation over a range of H₂ pressures (2.0-5.0 MPa) and temperatures (40-70 °C) using egg-shell Pd/Al₂O₃ (0.3 wt%) in a semi-batch reactor. A two site L-H mechanism was proposed that fits the experimental concentration profiles well. Accordingly, ethylbenzene was the sole product from the hydrogenation of styrene. The ethylbenzene as the major hydrogenated products in these studies, can be explained by the adsorption of the ethyl double bond of styrene on the catalyst surface, rather than the adsorption through the benzene ring of styrene [30]. Nijhuis et al. [12] examined styrene hydrogenation diluted in thiophene solvent (typically at 50 °C) and proposed a L-H model for styrene hydrogenation that is 1^{st} -order with respect to H₂ pressures up to 3 MPa, agreeing with previous studies by Chaudhari et al. [8]. The order of styrene, in some systems, changed from 0 to 1 [12, 14, 31], indicating the styrene hydrogenation mechanism might be L-H as the styrene adsorption term in the denominator

tends to "disappear" when the styrene concentration is low. Corvaisier et al. [14] investigated styrene hydrogenation using different metals supported on silica at 40 °C. 100% selectivity in ethylbenzene was detected over Cu, Pt, Pd, Co, Ni, and Rh catalysts and 3% ethylcyclohexane over Ru or Ir at 98% conversion of styrene. The reaction order was not clear in H_2 according to their results due to the fact that H_2 pressure was held constant.

A study done by Meille et al. [11] on the topic of α -methylstyrene (AMS) hydrogenation (an additional methyl group attached to the double bond of styrene, see Table 4), reported that L-H kinetics could be applied to AMS hydrogenation over the temperature range of 0-47 °C and pressure 0.1-0.6 MPa with 1 wt% Pd/Al₂O₃.

Reactant	Molecule structure	
Styrene	H ₂ C	
AMS	H ₂ C CH ₃	

Table 4. Styrene and AMS molecule structure comparison.

Also, they proposed 1^{st} -order in H₂ and 0-order in the AMS for hydrogenation kinetics. Cabello et al. [31] used Rh supported on AlPO₄ catalysts (0.25-1 wt%) over the temperature range 20-50 °C and pressure 0.45-0.7 MPa to investigate the AMS and styrene (methanol as the solvent) hydrogenation. Identical apparent rates and activation energies were found using the modified Horiuti-Polanyi mechanism, indicating that the additional methyl group may not contribute a significant effect on the hydrogenation. They suggested that the reaction order was 1st-order in H₂ and 0-order in AMS or styrene. However, the order of AMS varied from 0 to 1 depending on the conditions of the system [31]. Both studies concluded that cumene was the only hydrogenated product of AMS hydrogenation. Moreover, Meille et al. [11] noted that a trace amount of water severely affected the reaction rate due to the strong adsorption of water on the catalyst surface. By further investigations [32], they confirmed that this competitive adsorption existed between water and AMS.

As for the olefin hydrogenation, Boudart and Cheng [33] used Ni catalyst at 20 °C and 101 kPa to study cyclohexene hydrogenation diluted in cyclohexane. Since the turnover rate doubled as the exposed Ni increased from 29 to 66%, they reported the hydrogenation reaction order was 0 in cyclohexene and assumed 1/2 order in H₂. Qu and Prins [34] investigated cyclohexene hydrogenation over Ni-Mo-S (4 wt% Ni and 13 wt% Mo) supported on Al₂O₃ or amorphous silica alumina (ASA) catalysts at 5.0 MPa and 310-350 °C. A higher conversion of cyclohexene and selectivity to cyclohexane were observed using the Al₂O₃ support, whereas the ASA supported catalysts produced more isomerized products,

such as methylcyclopentene and methylcyclopentane due to lower Mo dispersion. According to their work, the L-H model was used to fit the concentration profiles in a broad range resulting in 0 to 1 order in H_2 when cyclohexene partial pressure was in a range of 16-100 kPa.

The competitive hydrogenation between diolefins and olefins is also observed in hydrotreators. Previous studies have shown that styrene hydrogenation is much faster than 1-octene hydrogenation [12, 35]. Nijhuis et al. [12] reported that the styrene hydrogenation rate constant was 140 mmol·g⁻¹·min⁻¹ compared with 40 mmol·g⁻¹·min⁻¹ for 1-octene hydrogenation at 50 °C. Zhou et al. [10, 13] also observed the same trend that the hydrogenation of styrene was faster than that of 1-hexene in a model PYGAS hydrogenation, indicating that olefin hydrogenation was suppressed under these experimental conditions.

In short, the diolefin or olefin (styrene, AMS, and cyclohexene) hydrogenation kinetics are generally based on a L-H mechanism [10-14, 34, 36] using Pd catalyst. The activation energies (Ea) for styrene hydrogenation varied from 15 to 55 kJ/mol [7, 8, 10, 12-14, 31] and for AMS hydrogenation from 25.9 to 38.7 kJ/mol [11, 31] (Tables 5-6). Noble metals are more active for diolefin hydrogenation (15-55 kJ/mol) due to relative low activation energies compared to other metals (Ni, 61 kJ/mol). Note that the units in Tables 5-6 can be found in

related literature.

The discrepancy of diolefin hydrogenation activation energies is due to various catalyst types and kinetic models. Few studies related to diolefin or olefin hydrogenation using metal sulfide catalysts are available. None of these propose clear diolefin hydrogenation as well as polymerization kinetics.

Catalyst, Pd wt%	Reaction condition	Kinetic equation	Ea (kJ/mol)	References
0.3	60-180 °C, 2.1-4.8 MPa H ₂	$r_{HYD} = k_{HYD}C_R^{a}$	15	[7]
0.1	15-45 °C, constant H ₂	$r_{HYD} = \frac{k_{HYD}C_{H_2}C_R}{(m_1 + m_2)^2} b$	55	[8]
	pressure	$(1+K_2C_R)^2$		[*]
0.1	18-60 °C, 3.5 MPa H ₂	complex rate expression	23	[14]
0.3	40-70 °C, 2.0-5.0 MPa H ₂	$r_{\rm HYD} = \frac{k_{\rm HYD}K_2C_R\sqrt{K_1C_{\rm H_2}}}{A_1A_2} \ ^{\rm c}$	30	[13]
0.3	40-70 °C, 2.0-5.0 MPa H ₂	$r_{\rm HYD} = \frac{k_{\rm HYD}K_2C_R\sqrt{K_1C_{\rm H_2}}}{A_1A_2} \ ^{\rm c}$	26	[10]
0.5	50-100 °C, 0.6 MPa ^d	$r_{HYD} = k_{HYD}C_{H_2} \frac{\kappa_2 c_R}{_{1+K_2}c_R + \kappa_{th}c_{th}} \ ^{\rm e} \label{eq:rhydrodynamical}$	54	[12]
Catalyst, Rh wt%	Reaction condition	Kinetic equation	Ea (kJ/mol)	References
Rh, 0.25-1	20-50 °C, 0.45-0.7 MPa H ₂	$r_{HYD} = k_{HYD} P_{H_2}$	27-31	[31]
Catalyst, Ni wt%	Reaction condition	Kinetic equation	Ea (kJ/mol)	References
Ni, 5	18-60 °C, 3.5 MPa H ₂	complex rate expression	61	[14]

Table 5. Styrene hydrogenation kinetics over several catalysts.

^a r_{HYD} : hydrogenation rate expression; k_{HYD} : hydrogenation rate constant; C_R : model reactant (styrene) concentration. ^b when all phenyl acetylene is consumed. C_{H_2} : dissolved H₂ concentration. ρ_b : catalyst bed density. K₂: Equilibrium constant of styrene. ^c $A_1 = 1 + \sqrt{K_1 C_{H_2}}$, where K₁ is equilibrium constant of H₂; $A_2 = K_2 C_R + K_{CPD} C_{CPD} + K_{HEX} C_{HEX}$, K_{CPD} and K_{HEX} refer to equilibrium constant of cyclopentadiene and 1-hexene, respectively. C_{CPD} and C_{HEX} refer to cyclopentadiene and 1-hexene concentration, respectively. ^d Temperature range is calculated based on the Arrhenius plot. ^e K_{th} is equilibrium constant of thiophene; C_{th} is thiophene concentration.

Catalyst, wt%	Reaction condition	Kinetic equation	Ea (kJ/mol)	References
Pd, 1	5-45 °C, 0.1-0.6 MPa H ₂	$r_{\rm HYD} = \frac{k_{\rm HYD} K_1 C_{\rm H_2}}{(1 + K_1 C_{\rm H_2})^2}$	39	[11]
Rh, 0.25-1	20-50 °C, 0.45-0.7 MPa H ₂	$r_{HYD} = k_{HYD} P_{H_2}$	27-31	[31]

Table 6. AMS hydrogenation kinetics over Pd or Rh catalysts.

1.2.3 Coke-precursors and coke formation

Catalyst deactivation during hydrotreating processes can be very complex since many deactivation mechanisms occur simultaneously and the deactivated catalysts are difficult to characterize [15]. In general, catalyst deactivation can be classified into five categories: poisoning, fouling (carbon deposition, coke formation), thermal degradation, loss of catalytic phases and attrition [19]. Poisoning usually occurs when unwanted compounds or impurities strongly chemisorb on the catalyst active sites and thus block the available sites or change the electronic or geometric environment of the catalyst surface. Thermal degradation takes place under high reaction temperatures (> 500 °C), causing the growth of the active metal crystallites or the loss of surface area due to the collapse of pores. Mechanical loss of catalyst activity includes reducing the catalyst size or breaking up the catalyst particles by attrition. Lastly, coke formation (fouling) occurs in the presence of diolefins, olefins and aromatics that tend to polymerize and form high molecular weight hydrocarbons that deposit on the catalyst surface. In addition, acidic sites on the catalyst surface expedite polymerization reactions to form coke precursors and coke [15]. The coke content is increased as the feed boiling range increases. Among the same boiling range hydrocarbons, aromatics and heterocyclics are considered as the coke precursor and conjugated diolefins are generally believed to be strong promoters of polymerization or gum formation reactions [37, 38].

In the present study, due to the relatively low reaction temperatures (≤ 250 °C) and short reaction time (≤ 510 mins), it is unlikely that coke (high C/H ratio hydrocarbons) forms during the reaction period. Instead, resinous, polymeric compounds (gum, low C/H ratio hydrocarbons) are formed after solvent washing [37, 39]. Gum composition and amount are dependent on the solvent used [40].

In hydrotreators, these carbonaceous materials deposited on the hydrotreating catalysts will result in (Fig. 5) [41]:





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- Blocking the reactant accessing into the pores.
- Covering all catalyst particles thus deactivating it.
- Gum (coke) is growing out of the pores and is extending into the reactor bed resulting in pressure build-up.

With metal sulfide catalysts, such as MoS₂, aromatics tend to be partially hydrogenated and form carbenium ions on those catalysts [15], which results in coke precursors being generated on acidic sites. Other unsaturated hydrocarbons will react with these species to grow the hydrocarbon chain and to form a new carbocation (carbenium ion) [42]. By repeating the chain-growing processes, a single molecule will polymerize into a high-molecular weight hydrocarbons (a detailed mechanism is shown in Fig. 6a and 6b).

-

Step 1: Reaction of olefin with Brønsted acid to form secondary carbenium ion: $H_2C = CHCH_3 + HX \implies CH_3 - CHCH_3 + X^-$ (1)

Step 2: Condensation reaction of a C_3 carbocation with a C_3 olefin to form a condensed, branched C_6 product with a carbenium ion:

$$CH_{3}-CHCH_{3} + H_{2}C = CHCH_{3} \xrightarrow{\qquad} CH_{3}-CHCH_{3} \qquad (2)$$

Step 3: Reaction of carbenium ion with Brønsted base to form olefin:

$$CH_3$$
 CH_3 CH_3 CH_3 (3)
 CH_3 - CH - CH_2 - CH - CH_3 + X - \checkmark CH_3 - CH - CH_2 - CH - CH_2 + HX

b. Cyclization from Olefins

Step 1: Formation of an allylic carbocation ion by reaction of a diene with a primary carbocation ion:

$$R_1^+ + R_2 - CH = CH - CH = CH - CH - CH_2CH_3 \rightleftharpoons$$

$$R_1H + (R_2 - CH - CH - CH - CH_2CH_3)^+ \qquad (4)$$

Step 2: Reaction of an allylic carbocation ion with a Brønsted base to form a triene: X^+ (R₂- CH \cdots CH \cdots CH \cdots CH- CH₂CH₂)⁺ \longrightarrow

Step 3: Cyclization of a triene to form a substituted cyclohexadiene:

$$\begin{array}{c} \overset{K_2}{\underset{H_3C-CH}{H_3C-CH}} \xrightarrow{K_2} \\ \overset{H_3C-CH}{\underset{CH}{H_3C-CH}} \xrightarrow{H_3C-CH} \\ \overset{H_3C-CH}{\underset{CH}{H_3C-CH}} \end{array}$$
(6)

Step 4: Formation of a tertiary carbocation ion:

.

. .

Step 5: Reaction of a tertiary carbocation ion with Brønsted base to form substituted

benzene:
$$\begin{array}{c} R_{2} \\ X^{*} + H_{3}C - CH \\ CH \\ CH \\ CH \\ CH \end{array} \xrightarrow{R_{2}} H_{3}C - CH \\ H_{3}C - CH$$

Figure 6a. Coke formation mechanism [41]. Reprinted with permission from Elsevier, Copyright (2001).

c. Formation of Polynuclear Aromatics from Benzene

Step 1: Initiation (protonation of benzene):

$$\underset{H}{\overset{H}{\overset{H}}}_{\overset{H}{\overset{H}}} \underset{H}{\overset{H}{\overset{H}}}_{\overset{H}{\overset{H}}} \overset{H}{\overset{H}} \overset{H}{\overset{H}} \overset{H}{\overset{H}} \overset{H}{\overset{H}} \overset{H}{\overset{H}} \overset{(9)}{\overset{(9)}}$$

Step 2: Propagation (condensation reaction of carbocation with benzene followed by H abstraction):



Figure 6b. Coke formation mechanism [41]. Reprinted with permission from Elsevier, Copyright (2001).

Weissman and Edwards [43] reported that less dense coke was detected after hydrotreating a naphtha feed compared to a heavier feed over Ni-Mo or Co-Mo catalysts. The catalysts were deactivated due to active sites being blocked by carbon deposition. Much research has been done related to coke precursors and/or coke formation using Pd catalysts. Lin and Chou [9] reported that during the hydrogenation of isoprene at 44 °C and 4.1 MPa, the egg-shell Pd (0.2 wt%, Pd/Al₂O₃) catalysts favored hydrogenation over coke formation. They also detected

some polymerization products in their experiments and the coke precursors were determined by GC-MS. In subsequent work on the hydrogenation of styrene, Zhou et al. [10, 13] found that none of the polymerization reactions was detected when using the egg-shell Pd catalysts. Additionally, Cheng et al. [7] reported that styrene hydrogenation over 0.3 wt% Pd/Al₂O₃ under high temperatures exhibits more polymerization; whereas Corvaisier et al. [14] found that there was no polymerization at low temperatures (0.09 wt% Pd on silica). These results have shown that the diolefin structures as well as the operating conditions play an important role in forming coke precursors or heavy hydrocarbons during diolefin hydrogenation.

Anderson et al. [30] used Ni supported on AlPO₄ catalyst and reported that hydrogenation and polymerization occurred in parallel, the latter reaction occurring on acidic sites of the catalytic surface. The order of reactivity during coke formation processes are polynuclear aromatics> aromatics> olefins> branched alkanes [41].

1.3 Conclusions

• Coker naphtha is a complex product that is unstable as it includes a significant quantity of unsaturated hydrocarbons, such as olefins, diolefins and aromatics, that tend to undergo polymerization reactions and carbon deposition causing reactor pressure build-up. Therefore, two stage hydrotreators are usually applied to remove these unwanted

hydrocarbons at low temperatures (~ 200 °C) to avoid polymerization. However, polymeric carbon deposition on the hydrotreating catalysts and pressure build-up may still occur.

- Hydrotreating catalysts include noble metals and metal sulfides. Metal sulfide catalysts are generally used in commercial hydrotreators, since the noble metals are very expensive and easily poisoned by S-containing compounds.
- Active hydrogenation sites for unpromoted and promoted metal sulfide catalysts are different and are related to cus metals.
- Few studies report diolefin hydrogenation kinetics over metal sulfide catalysts. Diolefin structure plays an important role in determining the reactivity and product selectivity of hydrogenation.
- The use of Pd catalysts to investigate the diolefin (styrene and AMS) hydrogenation kinetics has been well studied in the literature. The results show that the major product of styrene and AMS hydrogenation over Pd is ethylbenzene and cumene, respectively. The reverse reaction can be neglected.
- L-H models have been reported as the most suitable hydrogenation kinetic models for both styrene and AMS. The hydrogenation orders and activation energy depend on catalysts and kinetic models.
- With the help of acidic sites on the catalysts, gum (coke) is formed due to polymerization of diolefins based on carbenium ion mechanisms.

- The occurrence of diolefin polymerization depends on the operating conditions and catalyst properties. Polymerization of diolefins occurs simultaneously with hydrogenation as a parallel reaction.
- Few diolefin polymerization kinetic studies over Ni-Mo-S catalysts are available.
- The relationship between gum (coke) precursors and gum (coke) has not been well developed in previous research.

1.4 Objectives of this thesis

The aim of the present study is to determine diolefin hydrogenation and dimerization or polymerization kinetics over a Ni-Mo-S catalyst. Specifically, the effects of operating conditions, diolefin structure and the presence of olefins are investigated. Since coker naphtha composition is very complex, styrene and AMS were chosen as model compounds that would represent the reactivity of the diolefins present in naphtha. The compounds have aromatic structure, carbon numbers and boiling points similar to the diolefin molecules present in coker naphtha. The hydrogenation and dimerization reaction (gum precursor formation) mechanisms and kinetics will be determined based on the concentration profiles obtained from a batch reactor. The obtained hydrogenation and dimerization kinetics will be relevant to the aromatics in the naphtha feed since the model compounds have aromatic character. Competitive hydrogenation and polymerization between olefins and diolefins is also investigated by mixing the same amount of cyclohexene with AMS in AMS reactions. Finally, the relationship between the dimer concentration and the gum content (carbonaceous deposits) is examined. Results from this study contribute to improving the operation of commercial hydrotreators in the oilsands.

Chapter 2. Experimental

2.1 Experimental setup and design

The reactor system used to conduct the experiments consists of a gas supply, a 300 mL autoclave reactor with one baffle and a gas-inducing Rushton-type impeller (Parker Autoclave Engineers, EZE300), a sampling line (liquid outlet), and a control center with data collection software installed in the computer (see Fig. 7).



Figure 7. Reactor setup and data collecting system.

In Figure 7, the cooling water (CW) was used to cool the reactor after reaction. The control center was used not only to monitor the pressure through the pressure transducer (PT), mixing speed (MI) and reaction temperature by thermocouple (TT) during the reaction, but also logged signals of the stirring speed, reaction pressure (PI) and reaction temperature (TI1) every 5 seconds.

At the beginning of each experiment, the reactor was loaded with 100 mL of reactant solution consisting of a certain amount of model compound (styrene or AMS) diluted in decalin (solvent) and Ni-Mo-S/Al₂O₃ catalysts, provided by Syncrude Canada. The catalyst in the form of extrudates was ground to 44-63 µm and then dried overnight to remove water before use [32]. The catalyst composition and textural properties did not change following mechanical grinding. Detailed chemical and catalyst information are summarized as follows (Tables 7-8):

Chemicals	Purity	
Decalin	Sigma Aldrich (≥99%) or Alfa Aesar (≥98%).	
Styrene	Alfa Aesar, ≥99.5%	
AMS	Alfa Aesar, ≥99%	

Table 7. Model compound and solvent purity information.

BET surface area (m^2/g)	156
Pore volume (cm^3/g)	0.28
Pore size (nm)	7.22
Mo (wt%) ^a	10.0-16.7
Ni (wt%) ^a	0.8-4.7

Table 8. Ni-Mo-S/Al₂O₃ BET surface area, pore volume and pore size.

^a metal compositions are based on oxide state according to manufacturer MSDS

Once loaded with liquid reactants and catalysts, the reactor was firstly purged in N₂ for 15 minutes to remove air and then flushed with H₂ for another 15 minutes to remove N₂ from the system. Then the reactor was pressurized to 3.4 MPa (assuming no H₂ had been consumed before the temperature reached the desired reaction temperature) and heated up to the desired temperature at a ramp rate of 12 °C/min by a heating jacket (TI2) at a 1500 rpm stirring speed. As the reactor reached the desired temperature, the exothermic hydrogenation reaction and the slow damping of the temperature increase, caused the reaction temperature to fluctuate before reaching stability after about 8 minutes when heating to 200 °C. Higher reaction temperatures (225 and 250 °C) reduced this time to 7 and 6 minutes, respectively. The highest detected reaction temperatures for experiments at 200, 225 and 250 °C were nearly 210, 228, and 256 °C during fluctuation period, respectively.

During the course of the reaction, 1.75 mL liquid samples were drawn from the sampling line at certain time intervals (10 mins for the first five samples, 30 mins for the second last sample and 510 mins for the last sample) for GC-MS analysis. Prior to collecting each liquid sample, approximately 1-2 mL samples were drawn from the reactor sampling line that was purged in N₂. The liquid samples were analyzed by a Perkin Elmer (PE) gas chromatograph-mass spectrometer (Clarus 500 GC coupled with Clarus 560S MS). Details for the GC-MS system are given in Appendix A.1-A.8. The reaction liquid product collected after cool down of the reactor was analyzed by an Anton gum content tester using the standard ASTM method D381-12 to measure the gum content (details see Appendix A.9). Since the gas products were mainly H₂, the gas was not analyzed.

The reaction conditions for the styrene kinetic study were chosen based on an orthogonal design (Taguchi orthogonal arrays, Table 9) [44]. Constructing the three three-level factor orthogonal table ensures that the tested variables are statistically independent and reduces the total number of experiments from 27 to 9 due to its uniform distribution. The AMS kinetic study only considered reactant concentration and temperature as variables. Detailed operating conditions are shown in Table 10. Diene value was calculated based on Equation 1 from UOP326 method for industrial use, where MW refers to molecular weight (g/mol).

Diene value =
$$\frac{253.8 \times \text{reactant wt\%}}{\text{MW}}$$

Experimental #	Temperature °C	Styrene wt% ^a	Catalyst (g)
Xu 20140914	200	3.7	0.5
Xu 20140915	200	5.55	1
Xu 20140916	200	7.4	2
Xu 20140929	225	3.7	1
Xu 20141003	225	5.55	2
Xu 20140930	225	7.4	0.5
Xu 20141005	250	3.7	2
Xu 20141004	250	5.55	0.5
Xu 20141006	250	7.4	1

Table 9. Styrene reaction conditions based on orthogonal analysis (3.4 MPa H₂).

^a styrene wt% 3.7, 5.55, 7.4= diolefin (diene) value 9, 13.5, 18, respectively

Table 10. AMS reaction conditions based on single variable test over 0.2 g Ni-Mo-S catalyst

Experimental #	Temperature (°C)	AMS (wt%) ^a
Xu 20141108	200	4.2
Xu 20141109	250	4.2
Xu 20141117	200	4.2
Xu 20141201	225	4.2
Xu 20141202	225	6.3
Xu 20141203	200	6.3
Xu 20141206	250	6.3
Xu 20150120	200 with inhibitors	6.3

(3.4 MPa H₂).

^a AMS wt% 4.2, 6.3= diolefin (diene) value 9, 13.5, respectively

2.2 Mass transfer study

In all kinetic studies, it is important that the reactor operates within the kinetic regime in order to obtain intrinsic kinetics of the catalytic reaction. This section deals with gas-liquid (G-L) resistance (k_La), external and internal mass transfer resistance (k_ca and η , respectively) that might be encountered in the system.

Firstly, the effect of catalyst loading (gas-liquid resistance) was examined. Since the styrene conversion at 10 minutes increased approximately linearly with increasing catalyst mass in the range of 0.5 - 2g, the gas-liquid resistance was assumed negligible (Fig. 8) [8]. Note that the error in styrene conversion after 10 minutes reaction time was increased because of the temperature fluctuation described in Section 2.1.



Figure 8. Styrene conversion (mol%) as a function of catalyst weight, at T=200 °C, 3.7 wt% styrene diluted in decalin, R^2 =0.93.

Theoretical analysis of the reactor estimated a value of $k_La=1.64 \text{ s}^{-1}$ (Appendix B.1), at least 136 times higher than the highest styrene hydrogenation rate constant (0.012 s⁻¹) at 250 °C (assuming catalyst bed density (ρ_b) = 0.02 g/cm³, Table 14). Hence, the stirring speed was set

at 1500 rpm for all experiments to eliminate L-G mass transfer effects.

External mass transfer for the catalyst was excluded based on previous work conducted in similar systems (catalyst size below 63 μ m and 1500 rpm stirring speed) [45] and theoretical calculations (Appendix B.2). The k_ca was estimated as 0.034 s⁻¹, which is at least 3 times faster than the obtained styrene hydrogenation rate constant (0.012 s⁻¹) at 250 °C (assuming $\rho_b = 0.02$ g/cm³, Table 14). Hence we conclude that the external mass transfer is not a rate controlling step of the reactor system.

For the intra-particle resistance (internal mass transfer), the effectiveness factor was estimated as $\eta = 1$ (Appendix B.3), indicating that the internal resistance was minimal. The effectiveness factor was also confirmed experimentally by changing the catalyst particle size from 44-63 µm to 63-105 µm. The AMS conversion results have shown that by using the larger particles, the conversions after 40 and 70 minute reaction time were almost the same as that of smaller particles, indicating the internal mass transfer was negligible (Table 11). Detailed theoretical calculations are given in Appendix B.3.

Table 11. AMS conversion (mol%) as a function of time with two catalyst sizes, at 6.3 wt% AMS diluted in decalin, T=200 °C, 0.2 g catalyst.

Time (min)	Conversion mol% (44-63 µm)	Conversion mol% (63-105 µm)
40	20.4	20.8
70	32.2	30.2

In short, the above analysis shows that the conducted experiments were in the kinetic regime because the magnitude of the rate of each mass transfer process was significantly greater than the observed reaction rate, calculated from the measured reactant consumption and product formation.

2.3 Carbon balance and experiment repeatability and

The carbon recovery for the experiments was $82\pm7\%$ for the styrene experiments and $90\pm7\%$ for AMS (see details in Appendix C) based on GC-MS results. The relative standard deviation (RSD) for the AMS reaction conversions (mol%) was 2.8% and for the hydrogenated product cumene yield was 1.1%, indicating the reactor system was repeatable. The example calculations are given in Appendix D. However, note that significantly larger errors occurred for measuring the AMS dimer concentration. Although AMS dimer calibration data showed that the GC-MS AMS dimer analysis had errors that were $\pm3\%$ of

the measured concentration, repeat experiments showed that AMS dimer yields varied by as much as $\pm 88\%$ due to very low dimer yields and gum formation occurring during reaction.

2.4 Inhibition effects

Note that both model compounds contain 4-tert-butylcatechol as an inhibitor. The effect of inhibition was studied in the AMS reactions by washing the AMS through an aluminum oxide packed glass column to remove the inhibitor. Comparing the results with and without the inhibitor (Fig. 9), shows that the AMS conversion increased about 7% in the presence of the inhibitor, indicating that the inhibitor did not have a significant impact on the reactions. It should also be noted that for the styrene reactions, the inhibitor was not removed, whereas for all AMS reactions, the inhibitor was removed.



Figure 9. AMS conversion (mol%) as a function of time with and without inhibitors at T=200 °C, 6.3 wt%

diluted in decalin,0.2 g catalyst.

Chapter 3. Results and discussion

3.1 Styrene hydrogenation

Styrene may undergo several reactions in the presence of H₂, including hydrogenation, dimerization, polymerization and isomerization over Ni-Mo-S catalysts. However, for the experimental conditions of the present study, the major products were ethylbenzene and styrene dimers (mainly 1.3-diphenyl-butane and other isomerized dimers). Although other minor components were identified by GC-MS, such as ethylcyclohexane (~1% of detected ethylbenzene at 510 min), trimers (not detected at 510 min), their concentration was so low as to make quantification impractical. These minor compounds have not been considered in the kinetic analysis. Consequently, the data presented in this section are restricted to the main hydrogenation and dimerization products. Gum products are considered as dimer products undergoing further polymerization reactions producing higher molecular weight hydrocarbons and will be discussed as part of the dimerization analysis. Anderson et al. [30] reported that the polymerization and hydrogenation reactions occurred in parallel reactions, so that a similar reaction scheme was assumed in the present study as illustrated in Figure 10. It should be noted that styrene dimers (a-d) are calibrated using1,4-diphenyl-butane (see Appendix A.7).



Figure 10. Proposed reaction pathways for the hydrogenation and dimerization and polymerization of styrene (a) ethylbenzene (b) 1, 3-diphenyl-butane (c) 1-methyl-2-phenylpropylbenzene (d)

1-(2-ethylphenyl)-1-phenylethane (e) 1,3-diphenyl-1-butene.

For each set of conditions (see Section 2.1), the liquid samples were drawn periodically for component analysis to yield the concentration-time profiles that have been used for the kinetic analysis (see Figs.11-13; dimer profiles are shown in Section 3.5). It should be noted that although the initial hydrogen pressure for each experiment was different, the H_2 pressure was about 3.4 MPa (typical H_2 pressure in real hydrotreators) once the reactor reached reaction temperature, despite the fact that some of the H_2 might be consumed during the temperature ramp. Also, H_2 was always in excess even when all reactant was hydrogenated to ethylbenzene.



Figure 11. Experimental concentration data versus reaction time at (a) T=200 °C, 3.7 wt% styrene diluted in decalin, 0.5 g catalyst. (b) T=200 °C, 5.55 wt% styrene diluted in decalin, 1 g catalyst. (c) T=200 °C, 7.4 wt% styrene diluted in decalin, 2 g catalysts. (■ styrene, ▲ ethylbenzene).



Figure 12. Experimental concentration data versus reaction time at (d) T=225 °C, 3.7 wt% styrene diluted in decalin, 1 g catalyst. (e) T=225 °C, 7.4 wt% styrene diluted in decalin, 0.5 g catalyst. (f) T= 225

°C, 5.55 wt% styrene diluted in decalin, 2 g catalysts. (
styrene,
ethylbenzene).



Figure 13. Experimental concentration data versus reaction time at (g) T=250 °C, 5.55 wt% styrene diluted in decalin, 0.5 g catalyst. (h) T=250 °C, 3.7 wt% styrene diluted in decalin, 2 g catalysts. (i) T=250

°C, 7.4 wt% styrene diluted in decalin, 1 g catalyst. (
styrene,
eta ethylbenzene).

These profiles show that all styrene was consumed within 20 minutes for most of the trials, indicating that data analysis should be selected within 10 minutes since styrene had not been completely consumed before that time. Table 12 reports the styrene conversion and product selectivity after 10 minutes when the reaction reached the desired reaction temperature.

Temperature (°C)	Stymono (wt0/)	Cataluat (a)	Styrene conversion	Ethylbenzene	Styrene dimer
	Styrene (wt%)	Catalyst (g)	(mol%)	(mol%)	(mol%)
200	3.7	0.5	43	97.2	2.8
200	5.55	1	61	98.9	1.1
200	7.4	2	82	99.0	1
225	3.7	1	97	97.3	2.7
225	7.4	0.5	88	98.7	1.3
225	5.55	2	69	97.0	3.0
250	5.55	0.5	95	98.4	1.6
250	3.7	2	85	96.3	3.6
250	7.4	1	76	91.6	8.4

Table 12. Styrene reaction conversion and product selectivity over Ni-Mo-S catalysts at various reaction conditions.

Assuming that thermal reactions would not convert much of styrene to other products (Fig. 14, AMS thermal reaction, conversion <3.3 mol% at 70 mins), the reported conversion and selectivity values are net of thermal reactions.



Figure 14. Experimental concentration data versus reaction time at T=200 °C, 6.3 wt% AMS (6.2 mol/cm³) diluted in decalin (◀ AMS ▷ cumene).

Table 12 shows that the highest styrene conversion was achieved at 225 °C with one gram of catalyst and 3.7 wt% styrene concentration. The highest selectivity to ethylbenzene was obtained at 200 °C with two grams of catalysts and 7.4 wt% styrene concentration. The highest styrene dimer concentration occurred at 250 °C with one gram of catalyst and 18 diene value reactant (7.4 wt% styrene concentration).

Since the styrene experiments were done using orthogonal analysis, comparing results from three variables (temperature, styrene concentration, and catalyst amount) was challenging. To solve this problem, a mathematical approach was used to process the time-concentration profiles. For instance, by averaging the ethylbenzene concentration at each reaction temperature (200, 225, 250 °C), one can detect which temperature affects the reaction most, regardless of the other two tested variables (catalyst amount, styrene concentration). The same analysis method would apply to the other two parameters. As a result, a combination of three variables was obtained to determine the operating conditions that have the greatest effect on the styrene reactions.

3.2 Effect of operating conditions on styrene hydrogenation

The effect of operating conditions on the average ethylbenzene concentration over the Ni-Mo-S catalyst after 10 minute reaction is shown in Figures 15-17.


Figure 15. Average ethylbenzene concentration as a function of reaction temperature.



Figure 16. Average ethylbenzene concentration as a function of catalyst mass.



Figure 17. Average ethylbenzene concentration as a function of styrene concentrations (diene value).

Figure 15 shows that styrene hydrogenation occurred at relatively low reaction temperature of 200 °C. As the temperature increased to 250 °C, about 6.5% increase in hydrogenated products was observed, suggesting that temperature might not be the most important parameter influencing the styrene hydrogenation. The effect of catalyst amount, as shown in Figure 16, reveals that increasing the catalyst loading increased the yield of hydrogenated products. The hydrogenated products increased by 35% over the range of catalyst mass examined (Fig. 16). The effect of styrene concentration (3.7-7.4 wt% styrene, Fig. 17) shows that higher concentration resulted in higher yield of hydrogenated products (57% increase). Based on these results, it seems that the catalyst amount and styrene concentration have major effects on the hydrogenation compared to the changes in the reaction temperature, over the range of

operating conditions studied.

ANOVA analysis was used to confirm the significance of the effects of operating conditions on hydrogenation. Table 13 reports the AVOVA analysis results (calculations see Appendix E). The F value of styrene concentration (19.54) was the only variable larger than $F_{critical}$ (= 9), indicating that styrene concentration affected the hydrogenation in a statistically significant way. Catalyst mass and temperature were not statistically significant although the F values show that the styrene concentration had more of an effect than temperature, agreeing with the results from Figures 15 and 16.

Variables	F value	F _{critical}
Temperature	0.37	9
Catalyst mass	7.61	9
Styrene wt%	19.54	9

Table 13. ANOVA analysis for styrene hydrogenation ($\alpha = 0.1$)

3.3 Styrene hydrogenation kinetics

The styrene hydrogenation kinetics is discussed in this section. During the course of reaction, the S content of the catalyst was assumed to remain constant for all trials due to the short reaction time and low reaction temperatures studied. Although there may be two different sites for H_2 and reactant adsorption, the difference of two sites can be considered as insignificant and it can be neglected to simplify the kinetic analysis [15]. Furthermore, H_2 is generally believed to undergo dissociative adsorption on hydrotreating catalysts [15].

Hence, based on the literature results and assumptions made above, a L-H mechanism [10, 12-14, 36] was used to describe the hydrogenation reaction, as shown in Equations 2-6. The production of C_{R2H} (ethylbenzene) was assumed to be the rate determining step (Equation 5) for the hydrogenation. The pseudo steady-state approximation was applied for the formation of the reaction intermediates: $C_{H\cdot S_V}$, $C_{R\cdot S_V}$ and $C_{RH\cdot S_V}$ in the reaction pathway. The final hydrogenation rate can be derived as shown in Equation 6. In order to simplify the work, the denominator was assumed to be 1 since $\sqrt{K_1C_{H_2}} \ll 1$ [8, 10], and $K_3K_2C_R\sqrt{K_1C_{H_2}} \ll K_2C_R \ll 1$ (K₂ was about 0.007; this value was calculated based on Pd catalyst at 200 °C [10]). Finally, the rate expression was modified to Equation 7 with the other terms that are incorporated into the hydrogenation rate constant (k_{HYD} , H₂ was in excess). In short, 1st-order kinetics with respect to the model reactant and 0-order in H₂ was used to describe the styrene

hydrogenation (Equation 7).

$C_{H_2} + 2S_v \leftrightarrow 2C_{H \cdot S_v}$	Equation 2
$C_R + S_v \leftrightarrow C_{R \cdot S_v}$	Equation 3
$C_{R \cdot S_{v}} + C_{H \cdot S_{v}} \leftrightarrow C_{RH \cdot S_{v}} + S_{v}$	Equation 4
$C_{HR\cdot S_v} + C_{H\cdot S_v} \rightarrow C_{R2H} + 2S_v$	Equation 5
$r_{HYD} = \frac{k_4 K_3 K_2 K_1 C_R C_{H_2} C_t^2}{(1 + K_3 K_2 C_R \sqrt{K_1 C_{H_2}} + K_2 C_R + \sqrt{K_1 C_{H_2}})^2}$	Equation 6
$r_{HYD} = k_{HYD}C_R$	Equation 7
C_{H_2} : dissolved H ₂ concentration, mol/cm ³	
S_v : vacant sites , mol/gcat	
$C_{H \cdot S_v}$, $C_{R \cdot S_v}$, $C_{RH \cdot S_v}$: adsorbed H ₂ , styrene, and intermediates, respectively, mol/gcat	
C_R : styrene concentration, mol/cm ³	
C_{R2H} : ethylbenzene concentration, mol/cm ³	
K_1, K_2, K_3 : adsorption equilibrium constants of H_2 , styrene and $C_{R \cdot S_v}$, respectively, cm ³ /r	nol
Ct: total available sites, mol/gcat	
r_{HYD} : hydrogenation rate expression, mol·min ⁻¹ ·g ⁻¹	
k_{HYD} : hydrogenation rate constant, cm ³ ·min ⁻¹ ·g ⁻¹	

3.4 Hydrogenation apparent rate constant and activation energy

The simplified styrene hydrogenation rate expression along with the batch reactor design equation were applied (Equation 8) to the measured data to estimate the apparent hydrogenation rate constants at three reaction temperatures and the apparent activation energy (Table 14). Considering the small amount of dimers formed initially (see dimerization concentration profiles in Figures 20-22), it was assumed that styrene was only converted to the hydrogenated product, ethylbenzene, at the beginning of the reaction (10 mins) to estimate the hydrogenation rate constants

$$x = 1 - \exp^{-\rho_b \cdot k_{HYD} \cdot t}$$

x: styrene conversion $\rho_{\rm b}$: catalyst bed density, g/cm³

t: reaction time, min

Temperature (°C) Rate constant (cm³·min⁻¹·g⁻¹) 200 13.08 ± 4.34 225 25.17 ± 9.19 250 37.43^{a} Activation energy (Ea, kJ/mol) 45.28 ± 2.39^{b}

Table 14. Styrene hydrogenation rate constant results.

^a data from Xu20141004. ^b based on Origin fitting standard error value.

Equation 8

Note that the k values reported in Table 14 were obtained after averaging k from all trials at the same temperature. The apparent activation energy (Ea) of styrene hydrogenation is about 45 kJ/mol (Fig. 18) by using the Arrhenius law (Equation 9) which is within the reported values (15-54 kJ/mol) using palladium catalysts.

$$k_{HYD} = k_0 e^{-\frac{E_a}{RT}}$$

 k_0 : pre-exponential factor, $cm^3 \cdot min^{-1} \cdot g^{-1}$

R: gas constant, 8.314 J·K⁻¹·mol⁻¹

T: reaction temperature, K



Figure 18. Styrene hydrogenation activation energy data fitting at 200, 225, and 250 °C , R²=0.99.

Parity plots (Fig. 19) and ANOVA analysis (Table 15) were used as validity checks for the

Equation 9

proposed model. Since the F-value is less than the F-critical value, it suggests that the model is valid.



Figure 19. Styrene hydrogenation parity plots at (a) T=225 °C, 7.4 wt% styrene diluted in decalin, 0.5 g catalyst. (b) T=200 °C, 3.7 wt% styrene diluted in decalin, 0.5 g catalyst. (c) T=200 °C, 3.7 wt% diene

diluted in decalin, 0.8 g catalyst. (\Box experimental styrene + modeled styrene).

Experimental	Temperature	Styrene	Catalyst (g)	F _{value}	E
	(°C)	(wt%)			Γcritical
a	225	7.4	0.5	0.0012	5.99
b	200	3.7	0.5	0.0071	5.32
с	200	3.7	0.8	0.0025	5.32

Table 15. Styrene hydrogenation parity plots ANOVA analysis results.

3.5 Styrene dimerization

Gum (coke) formation on metal sulfide catalysts is thought to involve gum (coke) precursors formed on acidic sites that are further converted to high molecular weight hydrocarbons [19, 41]. The styrene dimer in this study is assumed to act as a gum (coke)-precursor. At the end of the reaction (510 mins), the dimer concentration was compared to the amount of gum detected in the reactor liquid product, which served as an indicator of polymeric hydrocarbons. The dimer concentration profiles that were used for the kinetic analysis are shown in Figures 20-22.



Figure 20. Styrene dimer concentration data versus reaction time at (a) T=200 °C, 3.7 wt% styrene diluted in decalin, 0.5 g catalyst. (b) T=200 °C, 5.55 wt% styrene diluted in decalin, 1 g catalyst. (c)

T=200 °C, 7.4 wt% styrene diluted in decalin, 2 g catalysts.



Figure 21. Styrene dimer concentration data versus reaction time at (d) T=225 °C, 3.7 wt% styrene diluted in decalin, 1 g catalyst. (e) T=225 °C, 7.4 wt% styrene diluted in decalin, 0.5 g catalyst. (f) T=225

°C, 5.55 wt% styrene diluted in decalin, 2 g catalysts.



Figure 22. Styrene dimer concentration data versus reaction time at (g)T=250 °C, 5.55 wt% styrene diluted in decalin, 0.5 g catalyst (h) T=250 °C, 3.7 wt% styrene diluted in decalin, 2 g catalysts (i) T=250

°C, 7.4 wt% styrene diluted in decalin, 1 g catalyst

The styrene dimerization reaction data were processed based on the averaging method used for styrene hydrogenation to ethylbenzene (10 mins, see Figs. 23-25).



Figure 23. Average styrene dimer concentration as a function of reaction temperatures.



Figure 24. Average styrene dimer concentration as a function of styrene concentration (diene value).



Figure 25. Average styrene dimer concentration as a function of catalyst mass.

These data show that reactor temperature played an important role in producing dimers (Fig. 23). Results show that as the reaction increased from 200 to 250 °C, the dimer concentration in the product increased 3-fold. Similarly the highest amount of dimers was generated with the highest styrene concentration in the feed (Fig. 24). Interestingly, it seems that the medium catalyst weight led to the highest dimer content—1.49E-05 mol/cm³ (Fig. 25). The dimer content in 0.5 g and 2.0 g catalyst experiments was 7.29E-06 and 6.96E-06 mol/cm³, respectively. In contrast, when single variable test of catalyst weight were performed at 200 °C, the results displayed a different trend, indicating that more catalyst led to a higher concentration of dimers in the product (Fig. 26).



Figure 26. Styrene dimer concentration as a function of catalyst mass at 200 °C.

The difference in trends shown in Figure 25 and Figure 26 may be due to the averaging of dimer concentration over a range of conditions. Further investigation needs to be done to study the effect of catalyst mass on styrene dimer formation. Based on these results, it seems that the temperature and styrene concentration play the most significant role in determining dimer concentration in the product.

ANOVA analysis was applied to determine the statistical significance of these variables on styrene dimerization. Table 16 reports the AVOVA analysis results. Although the F values of three variables were less than $F_{critical}$ (9), indicating no significant effects, the dimerization was affected mostly by styrene concentration and temperature (Table 16) due to higher F values (6.41 and 2.24, respectively). The catalyst mass was of least importance.

Variables	F value	F _{critical}
Temperature	2.24	9
Catalyst mass	1.73	9
Styrene wt%	6.41	9

Table 16. ANOVA analysis for styrene dimerization ($\alpha = 0.1$)

Analysis of the liquid product gum content, after the end of each relative test, is shown in Figure 27, plotted against the liquid dimer concentration.



Figure 27. Gum content as a function of styrene dimer concentration in the reaction liquid product.

Figure 27 clearly shows that a higher dimer concentration results in a higher gum content of the reactor liquid product, which supports the notion that the polymeric carbon (gum) that occurs on hydrotreating catalysts is formed at higher dimer concentration conditions in the reactor.

3.6 Dimerization apparent rate constant and activation energy

Dimer formation might be related to the catalysts which have weak acidic sites that activate the vinyl group of the styrene to form a carbenium-like molecule [15]. Then, another reactant attacks to this ion to form a dimer. New dimers might undergo other reactions, such as isomerization or gum formation. However, the mechanism for dimer formation is not clear from this study due to the small amount of dimers presented at all reaction conditions and lack of literature support. The dimerization rate can be assumed to be determined by the rate of attack by the surface carbenium ion on the reactant. Therefore, pseudo 1st-order in styrene kinetics was applied to estimate a dimerization rate constant (Equation 10) as well as the activation energy (Fig. 28). Note that the styrene concentration used here was calculated from the styrene hydrogenation rate expression.

$$C_{D} = \frac{k_{Dimer} \cdot C_{A0}(1 - e^{k_{HYD}\rho_{b}t})}{k_{HYD}\rho_{b}} + C_{D0}$$

Equation 10

 C_D : dimer concentration, mol/cm³ C_{A0} : initial styrene concentration, mol/cm³ C_{D0} : initial styrene dimer concentration, mol/cm³ k_{Dimer} : dimerization rate constant, cm³·min⁻¹·g⁻¹



Figure 28. Styrene dimerization activation energy data fitting at 200, 225, and 250 °C, R²=0.96.

The rate parameters and activation energy are summarized in Table 17.

Temperature (°C)	Rate constant ($cm^3 \cdot min^{-1} \cdot g^{-1}$)	
200	0.18 ± 0.08	
225	0.44 ± 0.09	
250	1.82 ^a	
Activation energy (Ea, kJ/mol)	99.64 ± 8.85^{b}	

 Table 17. Styrene dimerization rate constant results.

^a data from Xu20141006. ^b based on Origin fitting standard error value.

Both styrene dimer parity plots (Fig. 29) and ANOVA tests prove that the pseudo 1st-order in styrene kinetics is valid for styrene dimerization (Table 18).



Figure 29. Styrene dimerization parity plots at (a) T=200 °C, 3.7 wt% styrene diluted in decalin, 0.5 g catalyst. (b) T=225 °C, 7.4 wt% styrene diluted in decalin, 0.5 g catalyst. (c) T=200 °C, 3.7 wt% diene diluted in decalin, 0.8 g catalyst. (* experimental styrene dimer O modeled styrene dimer).

Experimental	Temperature (°C)	Styrene (wt%)	Catalyst (g)	F _{value}	F _{critical}
а	200	3.7	0.5	0.012	5.32
b	225	7.4	0.5	0.00081	5.99
С	200	3.7	0.8	0.27	5.32

Table 18. Styrene dimerization parity plots ANOVA analysis.

Comparing the styrene hydrogenation parameters (k_{HYD} and activation energy) to dimerization values (see Table 19), confirms that the assumption made in Section 3.4 that the dimerization reaction rate was negligible compared to hydrogenation rate is valid, since the styrene hydrogenation rate was at least 21x's faster than dimerization.

Temperature (°C)	k_{HYD} (cm ³ ·min ⁻¹ ·g ⁻¹)	k_{Dimer} (cm ³ ·min ⁻¹ ·g ⁻¹)
200	13.1	0.18
225	25.2	0.44
250	37.4	1.82
E _a , kJ/mol	45.3	99.6

 Table 19. Styrene hydrogenation/dimerization kinetic parameter comparison.

3.7 AMS hydrogenation

AMS and styrene are much alike in chemical structure so that AMS may also undergo hydrogenation, dimerization, polymerization (gum formation), and isomerization. Under the conditions reaction in this study, and AMS dimers (mainly cumene 2,3-dimethyl-2,3-diphenylbutane and other isomerized dimers), were the major products. Although benzene-hydrogenated products were detected ($\leq 0.2\%$ of cumene at 510 mins), they were not used in the kinetic analysis due to their low concentration in the product. Hence only the hydrogenation of the isopropenyl group of AMS (selective hydrogenation) and dimerization (gum precursor formation) are discussed in this section. A comparable reaction scheme to that for styrene reactions was proposed as shown in Figure 30, on the basis that polymerization and hydrogenation occurred as two parallel reactions [30].



Figure 30. Proposed reaction pathways for the hydrogenation and dimerization and polymerization of AMS (a) cumene (b) 2,3-dimethyl-2,3-diphenylbutane (c) 1-phenyl-1,3,3-trimethylindan (d) Benzene, 1,1'-(1,3,3-trimethyl-1-propene-1,3-diyl)bis-.

Dimer compounds were calibrated and represented by 2,4-diphenyl-4-methyl-1-pentene (similar to AMS dimer structures) to simplify the analysis. Remembering that in styrene reactions the reactant was consumed within 20 minutes for most of the experimental conditions because the Ni-Mo-S catalyst was so active, a fixed amount of catalyst (0.2 g) was used in this section in order to generate sufficient kinetic data (see detailed concentration-time profiles in Figures 31-32. Dimer profiles are shown in the dimerization section).



Figure 31. AMS and cumene concentration data versus reaction time at (a) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (b) T=250 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (c) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (d) T=225 °C, 4.2 wt% AMS diluted in decalin, 0.2 g



Figure 32. AMS and cumene concentration data versus reaction time at (e) T=225 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (f) T=200 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (g) T=250 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (h) T=200 °C, 6.3 wt% AMS diluted in decalin with inhibitor, 0.2 g catalyst. (◀ AMS ▷ cumene).

The AMS conversion and the product selectivity after 70 minute reaction time (kinetic analysis range) are reported in Table 20. The thermal reaction was already considered and excluded so that the reported conversion and selectivity values are net of thermal reactions (see Fig.14). Table 20 reports that the highest AMS conversion was obtained at the highest

reaction temperature (250 °C) regardless of initial concentrations (4.2 or 6.3 wt% AMS). The selectivity to cumene was >92% for all trials, indicating that the Ni-Mo-S catalysts favor the AMS hydrogenation over dimerization under experimental conditions.

Experimental # Tem	Tomporoturo (°C)	ΔMS (wt%)	AMS conversion	Cumene $(mol\%)$	AMS dimer
	Temperature (°C)	AMS (wt/0)	(mol%)	Cumene (mor%)	(mol%)
А	200	4.2	66	92.3	7.7
В	250	4.2	100	98.7	1.3
С	200	4.2	62	99.5	0.5
D	225	4.2	86	99.0	1.0
Е	225	6.3	56	98.1	1.9
F	200	6.3	32	98.5	1.5
G	250	6.3	68	98.9	1.1
Н	200	6.3	40	95.1	4.9

Table 20. AMS reaction conversion and product selectivity over 0.2 g Ni-Mo-S at various reaction conditions (70 mins).

Unlike the data processing method used for the styrene study (orthogonal analysis), the data selected for the AMS hydrogenation were obtained over a 70 minute reaction period (kinetic analysis range) and was processed based on the AMS hydrogenated product cumene concentration as a function of reaction time. H₂ pressure was 3.4 MPa when the reactor reached the desired reaction temperature and was in excess for all experiments, as was the case for the styrene experiments.

3.8 Effect of operating conditions on AMS hydrogenation

The detailed cumene concentration profiles are shown in Figures 33-34. As the temperature increased from 200 °C to 250 °C, the cumene concentration increased by 77% at initial 4.2 wt% AMS concentration and by 75% with 6.3 wt% AMS, suggesting that the AMS hydrogenation was favored at higher reaction temperatures.



Figure 33. Cumene concentration comparison with 4.2 wt% AMS diluted in decalin, 0.2 g catalyst.



Figure 34. Cumene concentration comparison with 6.3 wt% AMS diluted in decalin, 0.2 g catalyst.

3.9 AMS hydrogenation kinetics

As stated above, the hydrogenation of the isopropenyl group of AMS was the only reaction pathway included in the kinetic analysis. The L-H model [11] was also applied and simplified to represent AMS hydrogenation kinetics as shown in Equation 7. Assumptions made for styrene hydrogenation were employed in AMS hydrogenation as follows:

- 1. The catalyst activity was assumed to be constant (sulfur content was assumed to be constant).
- 2. H₂ was assumed to undergo dissociative adsorption on the catalyst surface.
- 3. Same sites for both H_2 and reactant adsorption (C_R referred as AMS)
- 4. The rate determining step was Equation 5 (C_{R2H} was cumene in this case)
- 5. The pseudo steady-state approximation for three reaction intermediates $C_{H\cdot S_v}$, $C_{R\cdot S_v}$ and $C_{RH\cdot S_v}$ ($C_{R\cdot S_v}$ and $C_{RH\cdot S_v}$ were the adsorped AMS and intermediates, respectively)
- 6. The denominator was assumed to be 1 as a result of weak adsorption ($\sqrt{K_H C_{H_2}} \ll 1$ $K_3 K_2 C_R \sqrt{K_1 C_{H_2}} \ll K_R C_R \ll 1$)
- 7. Other terms are incorporated into the hydrogenation rate constant (k_{HYD})

In short, the AMS hydrogenation rate expression can be derived as per Equation 7, which is 0-order in H₂ while 1st-order in AMS.

3.10 AMS hydrogenation apparent rate constant and activation energy

Since only trace amounts of AMS dimers were detected in the reactor (see dimerization concentration profiles in Figures 40-41), the reactant consumption rate can be assumed to be equal to the hydrogenation rate to obtain the AMS hydrogenation rate constant. With 1st-order kinetics with respect to the AMS, along with the batch design equation (Equation 11), the rate constant was obtained from the slope of the plot of AMS concentration as a function of time (Figures 35-36).

 $\frac{dC_R}{dt} = k_{HYD} \cdot \rho_b \cdot C_R$

Equation 11



Figure 35. AMS hydrogenation 1st-order kinetic model fit at (a) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst, R²=0.95. (b) T=250 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst , R²= 0.99. (c) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst , R²= 0.74. (d) T=225 °C, 4.2 wt% AMS

diluted in decalin, 0.2 g catalyst, R²=0.96.



Figure 36. AMS hydrogenation 1st-order kinetic model fit at (e) T=225 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst , R²= 0.94. (f) T=200 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst , R²= 0.94.
(g) T=250 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst , R²= 0.95. (h) T=200 °C, 6.3 wt% AMS with inhibitor diluted in decalin, 0.2 g catalyst , R²=0.98.

Table 21 reports the AMS hydrogenation rate constants and ANOVA F values for each AMS parity plot (see Figures 37-38). The ANOVA analysis shown in Table 21 verifies that the AMS hydrogenation kinetic model is valid.

Note that two of the trials at the same reaction temperature (250 °C) show different reaction rate constants when the AMS concentrations are different. At the higher AMS concentration of 6.3wt%, a relatively low reaction rate is observed compared to with an AMS concentration of 4.3wt%. This may be a consequence of the fact that the hydrogenation reaction order in AMS may change since the denominator term in the L-H kinetic model that is a consequence of AMS adsorption will increase as the AMS concentration increases.

Experimental #	Temperature (°C)	AMS (wt%)	k_{HYD} (cm ³ ·min ⁻¹ ·g ⁻¹)	F _{value}	F _{critical}
А	200	4.2	6.37	0.31	4.96
В	250	4.2	33.9	0.0041	5.32
С	200	4.2	4.56	0.32	4.96
D	225	4.2	10.89	0.23	4.96
Е	225	6.3	5.24	0.21	4.96
F	200	6.3	2.48	0.38	4.96
G	250	6.3	7.58	0.16	4.96
Н	200	6.3	3.40	0.056	4.96

Table 21. AMS hydrogenation kinetic model parameter estimates over 0.2 g Ni-Mo-S catalyst at various reaction conditions.



Figure 37. AMS hydrogenation parity plots at (a) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (b) T=250 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (c) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (d) T=225 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (< experimental

+modeled).


Figure 38. AMS hydrogenation parity plots at (e) T=225 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (f) T=200 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (g) T=250 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (h) T=200 °C, 6.3 wt% AMS diluted in decalin with inhibitor, 0.2 g

catalyst. (◀ experimental + modeled).

The AMS hydrogenation activation energy (87.7 ± 22.8 kJ/mol) was estimated from Figure 39 using Arrhenius's law (rate constants are averaged at the same reaction temperature without the rate at 250 °C with 6.3 wt% AMS, Table 21), which is higher than reported values using Pd or Rh catalyst (25.9-38.7 kJ/mol) [11, 31].



Figure 39. AMS hydrogenation activation energy data fitting at 200, 225, and 250 °C, R²=0.94.

Comparing the apparent hydrogenation rate constants (Tables 14 and 21) and activation energy between styrene and AMS, clearly shows that the hydrogenation rate of styrene is faster than AMS at each reaction temperature. This difference is likely due to steric hindrance effects associated with the AMS. The "bigger" AMS molecule compared to the "smaller" styrene was "hindered" by the additional methyl group attached to the vinyl group that undergoes hydrogenation.

3.11 AMS dimerization

In contrast with styrene reactions, dimer formation from AMS was favored at lower reaction temperatures. Figure 40 shows that the maximum dimer content was detected at 200 °C with 4.2 wt% AMS.



Figure 40. Dimer concentration comparison at different reaction temperatures, 4.2 wt% AMS diluted in

decalin, 0.2 g catalyst.

The dimer formation was favored at 225 °C at the high initial AMS concentration (6.3 wt%,

Fig. 41), despite that the dimer content was close to dimers produced at 200 °C (510 mins). Additionally, comparing dimers produced at the same temperature but varied initial diene value, shows an absence of any significant effects of AMS concentration on dimer formation.



Figure 41. Dimer concentration comparison at different reaction temperatures, 6.3 wt% AMS diluted in

decalin, 0.2 g catalyst.

Figure 42 shows that less gum content was identified in AMS reactions compared to those using styrene (Fig. 27). This observation is likely due to steric hindrance effects that prohibit AMS dimers from undergoing further polymerization to yield gums.



Figure 42. Gum content as a function of AMS dimer concentration in the reaction liquid product.

3.12 Dimerization apparent rate constant and activation energy

Although the AMS dimerization mechanism is not known, it is generally believed that with the help of acidity from the catalyst, formation of carbenium-like ion is the key step to grow the hydrocarbon chain and thus to produce dimers and eventually high molecular weight compounds (gums). The pseudo 1st-order with respect to AMS kinetics for the dimerization was calculated using Equation 10, plotting the dimer concentration versus term D $(\frac{C_{A0}(1-e^{k_{HYD}\rho_b t})}{k_{HYD}\rho_b})$, Fig. 43, only four trials have reliable dimer data). Note that the AMS concentration was obtained from the AMS hydrogenation rate equation.



Figure 43. AMS dimerization pseudo 1st-order in AMS kinetic model fit at (a) T=250 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst, R²=0.66. (b) T=225 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst, R²=0.93. (c) T=225 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst, R²=0.96. (d) T=200 °C, 4.2 wt% AMS with inhibitor diluted in decalin, 0.2 g catalyst, R²=0.97.

Table 22 presents dimerization rate constants and ANOVA analysis F values based on the parity plots (Fig. 44). Since the F values are less than the critical F values, the pseudo 1st-order in AMS dimerization model is valid.

Experimental #	Temperature (°C)	AMS (wt%)	k _{Dimer} (cm ³ ·min ⁻¹ ·g ⁻¹)	F _{value}	F _{critical}
a	250	4.2	0.394	0.12	5.32
b	225	4.2	0.273	0.025	5.99
С	225	6.3	0.208	0.095	5.99
d	200	6.3	0.217	0.015	4.96

Table 22. AMS dimerization kinetic model parameter estimates over 0.2 g Ni-Mo-S catalyst at various reaction conditions.



Figure 44. AMS dimerization parity plots at at (a) T=250 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (b) T=225 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (c) T=225 °C, 6.3 wt% AMS diluted in decalin, 0.2 g catalyst. (d) T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g catalyst. (
(♦ modeled ♦ calculated).

The activation energy (24.2 ± 10.5 kJ/mol) was obtained from Figure 45 using Arrhenius law (rate constants from Table 22).



Figure 45. AMS dimerization activation energy data fitting at 200, 225, and 250 °C, R²=0.84.

The obtained AMS dimerization apparent activation energy seems relatively low compared to the styrene dimerization activation energy, due in part to the errors associated with measuring the AMS dimer product yield and the fact that only four trials with very low dimer yields were used to acquire the dimerization rate constants and activation energy. In order to assess the validity of the obtained AMS dimerization activation energy value, the uncertainty (u_{E_a}) associated with AMS dimerization activation energy calculation was obtained using Equation 12 [46].

$$u_{E_a} = 24.2 \sqrt{\frac{1-R^2}{R^2}} = 15.6 \text{ kJ/mol}$$
 Equation 12

The calculation shows that there is a large uncertainty in the AMS dimerization activation energy. Experiments with higher AMS concentrations would be needed to generate dimer concentration profiles with sufficient data so as to obtain more accurate rate constant estimates and hence, improve the accuracy of the R^2 value in the activation data fitting plot.

Since the AMS hydrogenation rate is at least 19'x faster than the dimerization rate, the assumption made in Section 3.9 is acceptable to be applied for the AMS hydrogenation rate constant calculation (Tables 23-24). The dimerization rate of styrene is higher than AMS at 225 °C and 250 °C, suggesting that the steric hindrance effects also play a role in determining dimer formation at higher reaction temperatures, as was observed for the hydrogenation reactions (Table 24). However, the dimerization rate of styrene is almost the same as AMS at 200 °C. The styrene dimerization rate decreased faster than AMS when the reaction temperature dropped from 225 °C to 200 °C because of the higher activation energy for styrene dimerization.

Temperature (°C)	Styrene, k_{HYD} (cm ³ ·min ⁻¹ ·g ⁻¹)	AMS ^a , k_{HYD} (cm ³ ·min ⁻¹ ·g ⁻¹)
200	13.1±4.3	4.2±1.5
225	25.2±9.2	8.0±2.8
250	37.4 ^b	33.9 ^c
Ea ^d (kJ/mol)	45.3±2.4	87.7 <u>±</u> 22.8

Table 23. Hydrogenation rate constant and activation energy comparison between styrene and AMS

^a reaction rates are averaged at the same temperature based on Table 19. ^b data from Xu 20141004.

^c data from Xu 20141119. ^d based on Origin standard error value.

Temperature (°C)	Styrene, k_{Dimer} (cm ³ ·min ⁻¹ ·g ⁻¹)	AMS ^a , k_{Dimer} (cm ³ ·min ⁻¹ ·g ⁻¹)
200	0.18 ± 0.08	0.22
225	0.44±0.09	0.24
250	1.82 ^b	0.39±0.03
Ea ^c (kJ/mol)	99.6±8.9	24.2±10.5

Table 24. Dimerization rate constant and activation energy comparison between styrene and AMS

^a reaction rates are averaged at the same temperature based on Table 20. ^b data from Xu 20141004.

^c based on Origin standard error value

3.13 The effect of olefin content

The competitive hydrogenation between diolefins and olefins was also examined using identical concentrations (4.2 wt%) of cyclohexene and AMS with 0.2 g Ni-Mo-S catalyst. The batch reactor concentration versus time data are summarized in Figures 46-48. Note that H_2 was in excess even if all cyclohexene and AMS were hydrogenated to cyclohexane and cumene, respectively.



Figure 46. Experimental concentration data versus reaction time at T=200 °C, 4.2 wt% cyclohexene and

AMS diluted in decalin, 0.2 g catalyst.



Figure 47. Experimental concentration data versus reaction time at T=225 °C, 4.2 wt% cyclohexene and

AMS diluted in decalin, 0.2 g catalyst.



Figure 48. Experimental concentration data versus reaction time at T=250 °C, 4.2 wt% cyclohexene and AMS diluted in decalin, 0.2 g catalyst.

Figure 46 shows that the cumene yield was almost the same as cyclohexane at 200 °C. As the temperature increased to 225 °C or 250 °C, the cumene concentration was increased 620% and 1400% (Figs. 47-48), respectively, but the cyclohexane increased 330% and 1100%, respectively, suggesting the cyclohexene hydrogenation was suppressed initially (70 mins). With prolonged reaction time (Fig. 49), the cyclohexane concentration exceeded the cumene (except 200 °C, identical quantities), indicating that the competitive hydrogenation exists between cyclohexene and AMS.



Figure 49. Cumene and cyclohexene comparison over 0.2 g Ni-Mo-S catalyst.

For the dimerization reaction, adding cyclohexene significantly reduced dimer content since cyclohexene or cyclohexane might adsorb on the acidic sites preventing AMS dimer formation (see Fig. 50). Note that the converted cyclohexene was all cyclohexane.



Figure 50. Dimer concentration comparison over 0.2 g Ni-Mo-S catalyst

As the involvement of cyclohexene disturbed reaction pathways and generated a more complex system, the kinetic parameters for hydrogenation and dimerization have not been determined.

Chapter 4. Conclusions and recommendations

4.1 Conclusions

Studies of diolefin hydrogenation kinetics, while plentiful, are predominantly focused on hydrogenation over noble metal catalysts. The hydrogenation kinetics of these unsaturated compounds over Ni-Mo-S catalysts, as well as the polymeric carbon deposit (dimerization or polymerization) issues that occur with coker naphtha hydrotreating processes, are rarely investigated,. The aim of the present thesis is to determine model compound (styrene and AMS as representative diolefins present in coker naphtha) hydrogenation and dimerization kinetics over metal sulfide catalysts.

Styrene reactions were based on orthogonal analysis. According to experimental results, the ethylbenzene and styrene dimers were the main products from styrene hydrogenation and dimerization, respectively. The selectivity to ethylbenzene was in a range of 91.6-99.0 mol% for all trials as the Ni-Mo-S catalyst mostly hydrogenated diolefins to alkanes. Styrene concentration and catalyst amount contributed the largest effect to hydrogenation, while styrene dimerization was mainly determined by temperature and styrene concentration.

Single variable tests were employed in AMS reactions by changing the temperature or AMS concentration. From the experimental results, the cumene and the AMS dimer were the major

products from the AMS hydrogenation and dimerization, respectively. The selectivity to cumene was 92.3-99.5 mol% for all trials, agreeing with the selectivity trend of styrene reactions. The reaction temperature affected the AMS reactions most. Higher reaction temperature increased the cumene yield, but reduced the dimer formation.

A simplified L-H model was proposed to describe the styrene or AMS hydrogenation reaction, which was 1st-order in reactant and 0-order in H₂. Due to the complexity of the system and the small amount of dimers formed with the help of acidity of the catalysts, a pseudo 1st-order in styrene or AMS kinetics for dimerization was derived. ANOVA analysis verified that all styrene and AMS hydrogenation and dimerization kinetic models were valid. The styrene hydrogenation reaction was much faster than dimerization, as was the case for AMS reactions. Comparing the activation energy values between styrene hydrogenation (45.3 kJ/mol) and dimerization (99.6 kJ/mol), the lower reaction "barrier" for hydrogenation led to a higher production of ethylbenzene, explaining the observed higher hydrogenation selectivity results. Although the value of AMS dimerization activation energy was small, limited kinetic data means that there is a large uncertainty associated with this activation energy. Comparing the hydrogenation rate constants, styrene was hydrogenated faster than AMS at each reaction temperature due to steric hindrance effects. With one methyl group less in styrene, the "smaller" molecule (styrene) was hydrogenated more easily than the larger molecule (AMS). The higher AMS hydrogenation activation energy (87.7 kJ/mol) further 99

supported this conclusion. The AMS dimerization rate was slower than styrene dimerization at higher reaction temperature (\geq 225 °C), showing that the steric hindrance effects also played a role in determining dimer formation.

Dimers also underwent gum formation reactions. The relationship between dimer concentration and gum content was established, and it showed that with more dimers produced, the higher the yield of gum produced in styrene reactions. This observation may explain the source of forming gum (polymeric hydrocarbons) causing the early shut down of hydrotreators. However, the gum content was not increased as dimer concentration increased in AMS reactions because of steric hindrance effects.

The competitive reactions between olefins and diolefins were observed by adding cyclohexene to the AMS reactant. Cyclohexane was identified as the only product from cyclohexene reactions. Adding olefin reduced the AMS dimer content, indicating that it might occupy the available acidic sites to prevent AMS dimers further undergoing gum formation reactions.

4.2 Recommendations

Different structures of diolefins in the coker naphtha feed, that may also cause catalyst deactivation in hydrotreating, should be considered in future work. Moreover, their interaction effects on catalyst fouling require further investigations, such as straight chain (conjugated and non-conjugated) diolefins mixed with cyclic diolefins.

In addition, catalyst characterization of the composition of the polymeric hydrocarbons is needed in future work, in order to propose a clearer reaction pathway to gum formation. Results from the characterization studies will benefit the development of the catalyst deactivation rate term for hydrogenation and dimerization kinetics. Thus a complete series of rate expressions can be developed to improve the kinetic models in the present study.

Finally, different metal sulfide catalyst configurations, such as varied S/Mo ratio or acidity, can be prepared to investigate the catalyst property effects on coker naphtha hydrotreating processes.

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Appendices

Appendix A Liquid sample analysis

A.1 GC-MS system

Liquid samples were collected using Agilent's certified 2 mL screw top vials with Silicone-Polytetrafluoroethylene-Silicone septa inserted with glass inserts. The samples were stored in a freezer to minimize any possible loss of easily-vaporized-hydrocarbons. These samples were then introduced into a PE GC-MS equipped with a PE autosampler (0.5 uL syringe) and Elite1 capillary column (length 30 m, film 0.25 mm, ID 0.25 mm) connecting to a PE TurboMass data processing terminal (see Fig. 51).



Figure 51. PE GC-MS (Clarus 500 GC-Clarus 560 MS) system with an autosampler.

The carrier phase used for all GC-MS tests was Praxair ultra high purity helium (99.999%), which assures a flat baseline and maximizes the usage of the GC column. After the carrier gas was connected to the system, all possible leak spots were tested using a Restek electronic leak detector (detect limit is 1×10^{-5} cm³/s) to obtain a leak-free analytical system.

A.2 GC-MS operating parameters and method

GC column saturation leads to the production of poor peak shape such as flat peaks, reducing the accuracy in measuring quantities. Moreover, the saturation of MS detector (MSD) will result in the absence of some peaks. Whether the saturation occurs in the GC column or in the MSD, it ultimately results in poor reproducibility. To avoid the GC column and MSD saturation, it is important to control the GC-MS operating parameters and methods, such as the volume of samples injected, the photomultiplier voltages, and the use of solvent delay during the analytical process.

Therefore, the operating parameters and the analytical programs were extensively modified to ensure all tests were done in the acceptable working range to obtain the concentration-time profiles that were both qualitatively and quantitatively reliable.

A.3 Carrier gas flow rate

The PE GC is equipped with electronic pneumatics, allowing it to control the flow rate, the linear velocity, and the pressure of carrier gas. According to Van Deemter plots, the column has the greatest efficiency (the height equivalent to a theoretical plate is at the maximum region) to separate injected samples as the linear velocity is within 20-40 cm/s. In all tests, the flow rate control mode was set to 1 mL/min ensuring that the linear velocity was within the optima region.

A.4 Split injection flow rates

The GC injection port is a traditional split/splitless injector. The switch between two modes depends on the volume or the sample concentration being injected. Selecting a proper split flow rate not only saves analytical time (easy to optimize and remove most of solvents), but also avoids column overloading and MSD saturation. Therefore, 0.2 uL of each liquid sample was introduced into the system with split flow rate at 250 mL/min (100 mL/min for styrene reactions), in other word, only 1/250 (1/100 for styrene reactions) of the injected volume actually entered into the column (see Table 25).

Compound	Density (g/cm ³)	Split flow (mL/min)	Actual injected mass
			(ng)
Decalin	0.909	50	3.584
		100	1.792
		250	0.717

Table 25. PE column splitflow/saturation calculation^a.

^a usually a column is capable of analyzing 50-100 ng injected samples

A.5 GC-MS system temperatures

The injection port temperature was set at 250 °C (320 °C for styrene) ensuring all thermo-labile compounds remained stable during analysis. In order to separate all compounds in the column successfully, it is critical to program a suitable oven temperature ramping method. Inappropriate programs such as isothermal analysis can result in wide broad peaks and rapid temperature increasing rate can lead to overlapping peaks. Based on that, the oven was initially set at 50 °C held for one minute then increasing up to 250 °C (320 °C for styrene) at a rate of 15 °C/min and finally held for 10 minutes at 250 °C (320 °C for styrene) to dispel impurities from the septum [47]. The oven programming was verified by using Restek Column resolution mixture (No. E1387) separating each compound successfully with good

resolution. The interface between GC and MS is a temperature-controlled transfer line and the temperature was set at the same as final oven programming temperature to eliminate any possible cooling spots as eluted compounds entered the MS.

A.6 Mass spectrometer method

The mass scan range was from 50 to 550 m/z covering the mass of major products of interests in the experiments. Low limit of mass eliminates impurities and reduce any possible errors during analysis. The heavier compounds in the liquid sample were about 500m/z. Therefore, this selected mass range satisfied the analytical requirements and reduced the machine burden. Since the forming of an entire peak needs 7-10 scans/s, scan time and inter-scan delay were set at 0.2 and 0.1 seconds for the two scan parameters, respectively.

A.7 GC-MS result repeatability and calibrations

The GC-MS result repeatability was determined by injecting one known concentration sample five times. The results were dealt by statistical analysis--the standard deviation (SD) and relative standard deviation (RSD) as shown in Equations 13-14, where x_i is the experimental value, \bar{x} is the averaged value, and Z is the number of repeat times. Since the RSD of the repeatability test was less than 0.026, the results from the system were repeatable.

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{Z - 1}}$$
Equation 13

$$RSD = \frac{s}{\bar{x}}$$
Equation 14

$$RF = \frac{A_{area}}{C}$$
Equation 15

The response factor (RF) is used to calculate the concentration based on the area from GC-MS analysis (Equation 15, where A_{area} = area, C= concentration). However, different chemicals have dissimilar RFs so that these values have to be obtained experimentally. Hence, external or single point calibration technique based on the suitability was applied to determine the RFs of reactants and products. It should be noted that not all calibrations of each compound in the liquid samples were prepared because some pure standards were not available in the market. Only standards of the reactants and products of interest were made to build the calibrations. Minor or pricey products (usually dimers) were quantified by using the established calibrations of compounds that have similar structures and compositions. Trace amounts of compounds (below the calibration lower limit) detected by GC-MS were not discussed in this thesis since it would not affect concentration-time profiles very much.

A series of standards were prepared based on the reactants and major products of interest. Each standard curve (except single point calibration) covers a range of tested concentrations from the beginning of the reaction to the end (510 mins). The standard was prepared using a Sartorius ME5 microbalance (one thousandth of a mg) or Shimadzu ATX224 (0.1 mg) to 116

measure different standard masses required to be diluted in the same mass of solvent (decalin for all tests), ensuring the accuracy of all prepared standards. All standards were stored in the freezer to ensure the consistency during analysis and each single standard was injected three times to check the reproducibility. It should be noted that each calibration curve was not forced going through the zero point due to systematic errors in the PE system.

The RSD for styrene was \pm 5.5% during the whole analytical period (14 days) using the single point test. The AMS dimer was also calibrated with single point test with RSD usually \leq 3%, although the RF of AMS dimer changed for each batch analysis due to a small amount of dimers formed during reaction. The R² of the calibration curves for all other compounds (styrene dimer, ethylbenzene, AMS, cumene, cyclohexane, and cyclohexene) were within 0.9515 and 0.9949, indicating that the analytic results were repeatable and valid. An example of AMS calibration curves (Fig. 52) and RF calculation (Table 26) is shown below:



Figure 52. An example of AMS calibration curves with R^2 =0.99.

AMS concentration, C (mol/mL)	Average area (A _{area})		
7.05E-05	2.8E07		
8.9E-05	3.5E07		
2.2E-04	8.9E07		
2.6E-04	1.1E08		
3.4E-04	1.4E08		
4.2E-04	1.6E08		
5.3E-04	2.0E08		
A _{area} = 3.7E11C+5.2E06			

Table 26. An example of RF calculation for AMS in Figure 52.
A.8 GC-MS sample scan

The GC-MS results from Tuobomass are in two forms: TIC (total ion chromatogram) and Mass spectra. The TIC form was used to quantitatively analyse compounds by adding up the fragmented ion intensities of compounds for the same run. In this form, X-axis represents the time (min) of the materials that are separated from the GC column and Y-axis reflects the added intensities of each compound. The area of each peak divided by response factor gives the real mass (or concentration) of that compound in the liquid sample (see Equation 15). Each peak presented in the mass spectrum form can be compared to the standard mass spectra library, such as NIST, to qualitatively identify the compound composition and structure. Figure 53 shows a TIC form of AMS reaction (6.3 wt %) performed at 225 °C with 0.2 g catalyst for a liquid sample collected at 510 min. The 4.61, 5.20, and around 12.73 mins are cumene, AMS, and AMS dimers, respectively.



Figure 53. TIC form for a liquid sample collected at 510 mins for the AMS reaction (6.3 wt%)

performed at 225 °C with 0.2 g catalyst.

A.9 Gum content test

At the end of each reaction, the liquid product was analyzed by Anton gum content tester (see Fig. 54) according to the standard method D381-12 to estimate the gum quantity.



Figure 54. Anton gum content tester.

A 50 ± 0.5 mL liquid sample was collected by a beaker and evaporated under steam 1000 ± 150 mL/s at 232-246 °C in the machine bath. After the evaporation and heptane ($\geq99.7\%$) washing, the remaining residue was reported as mg per 100 mL as defined in Equation 16. Table 27 reports an example of gum content calculation.

$$G = 2000(m_s - m_b)$$

G: gum content, mg/100mL

 $m_{s}{:}\ residue\ mass\ difference\ before\ and\ after\ analysis,\ g$

m_b: tare beaker mass difference before and after analysis, g

Table 27. An example of gum content calculation for styrene reactions at 200 °C, 1 g catalyst, and 5.55 wt%

	styrener	
m _s (g)	m _b (g)	G (g/100mL)
0.45	-3.8E-03	908

styrene.

Equation 16

Appendix B Mass transfer study

B.1 Gas-liquid mass transfer

The gas-liquid mass transfer coefficient k_La was estimated using Equations 17-20 for slurry bench top autoclave [48-50]. The Re number is a ratio of inertial forces and viscous forces; the Sc number is a ratio of momentum diffusivity and the mass diffusivity; the Weber number is a ratio of solvent inertia and surface tension.

$k_{\rm L}a = \frac{0.0141 {\rm Re}^{0.67} {\rm Sc}^{0.5} {\rm We}^{1.29}}{{\rm d}_{\rm ST}^2}$	Equation 17
$Re = \frac{\rho N_T d_{ST}^2}{\mu}$	Equation 18
$Sc = \frac{\mu}{\rho D_{H_2}}$	Equation 19
We = $\frac{\rho N_T^2 d_{ST}^3}{\gamma}$	Equation 20
$k_{L}a$: gas-liquid mass transfer resistance, s ⁻¹	
Re: Reynold's number, dimensionless	
Sc: Schmidt number, dimensionless	
We: Weber number, dimensionless	
d _{ST} : stirrer diameter, m	
ρ : decalin density, kg/m ³	
N_{T} : stirrer speed, s ⁻¹	
μ : decalin viscosity, kg·m ⁻¹ ·s ⁻¹	
D_{H_2} : H ₂ diffusivity in decalin, m ² /s	
γ: Decalin surface tension, N/m	

Parameter values for G-L resistance calculation are shown in Table 28. The result value (1.64 s⁻¹) is 136 times higher than the styrene hydrogenation rate constant (0.012 s⁻¹) at 250 °C (assuming $\rho_b = 0.02$ g/cm³, Table 14), indicating that the G-L resistance was minimal.

Parameter	Value
d _{ST} , m	0.0317
ρ^{a} , kg/m ³	880 ^b
N, s ⁻¹	25
μ^{c} , kg·m ⁻¹ ·s ⁻¹	0.003 ^d
$D_{H_2} m^2/s$	1.93E-09 ^e
γ, N/m	0.03^{f}
Re, dimensionless	7369
Sc, dimensionless	1766
We, dimensionless	584
k_La, s^{-1}	1.644

Table 28. Parameter values for estimating k_La .

^{a, c} dilute solution, use decalin viscosity and density instead. ^{b,d} values from Alfa Aesar MSDS.

^e calculated from [51]. ^f values from [52].

B.2 External mass transfer

The external mass transfer coefficient $k_c a$ was determined by Equations 21-24 [53-55], where A and B represent styrene and decalin, respectively. In order to simplify the calculation work, the condition was set at 20 °C, as the $k_c a$ will increase when the temperature is increased.

$$(\frac{k_{c}d_{p}}{D_{AB}})^{2} = 4.0 + 1.21N_{pe}^{2/3}$$
Equation 21

$$N_{pe} = \frac{gd_{p}^{3}\Delta\rho}{18\mu}$$
Equation 22

$$D_{AB} = 7.4 * 10^{-8} \frac{\sqrt{\phi_{B}M_{B}T}}{\mu \tilde{V}_{A}^{0.6}}$$
Equation 23

$$a = \frac{6m}{\rho_{p}d_{p}}$$
Equation 24

d_p: catalyst particle diameter, m

 D_{AB} : diffusivity of A in B, m²/s

 $\frac{k_c d_p}{D_{AB}}$: Sherwood number, dimensionless

N_{pe}: Peclet number, dimensionless

g: gravity, m/s^2

 $\Delta \rho$: density difference between particle and solution, $\rho_p - \rho$, kg/m³

 ρ_p : catalyst particle density, kg/m³

 ϕ_B : association parameter, 1 for decalin

M_B: decalin molecular weight, kg/mol

 \tilde{V}_A :styrene molar volume, m³/mol

a: external surface area of particles, m

m, catalyst loading, kg/m³

Parameter values for external mass transfer calculation are shown in Table 29

Parameter	Value
\tilde{V}_A , m ³ ·mole ⁻¹	1.15E-04 ^a
$D_{AB}, m^2 \cdot s^{-1}$	7.82E-09
g, $\mathbf{m} \cdot \mathbf{s}^{-2}$	9.8
d _p , m	7.4E-05 ^b
$\rho_p, kg \cdot m^{-3}$	1333
m, kg·m ⁻³	2
Peclet	4.26
Sherwood	7.18
$k_c, m \cdot s^{-1}$	2.83E-04
a, m ⁻¹	122
k_ca, s^{-1}	0.0344

Table 29. Parameter values for estimating k_ca.

^a values are from Alfa Aesar MSDS. ^b 200 mesh

The estimated k_ca value is 3 times higher than the fastest styrene hydrogenation rate constant (0.012 s⁻¹) at 250 °C (assuming $\rho_b = 0.02$ g/cm³, Table 14). Therefore, the external mass transfer effect was negligible.

B.3 Internal mass transfer

In terms of internal mass transfer effect, the effectiveness factor was evaluated by Equations 25-27 for the 1st-order reaction [56].

$$\eta = \frac{3}{\varphi_1^2} (\phi_1 \coth \phi_1 - 1)$$
Equation 25
$$\phi_1^2 = \frac{k_{HYD} d_p^2}{4D_e}$$
Equation 26
$$D_e = \frac{D_{AB} \phi_p \sigma_c}{\tilde{\tau}}$$
Equation 27

 η : effectiveness factor, dimensionless

- $Ø_1$: Thiele modulus for the 1st-order reaction, dimensionless
- D_e : effective diffusivity, m²/s
- φ_p : pellet porosity, 0.4, dimensionless
- σ_c : constriction factor, 0.8, dimensionless
- $\tilde{\tau}$: tortuosity, 3.0, dimensionless

The effective diffusivity was used to describe average diffusion inside the catalyst particle. Three typical values for the tortuosity, particle porosity, and constriction factor were selected from Fogler's book [56] to calculate the effective diffusivity. The Thiele modulus is a dimensionless number to measure the ratio of the internal diffusion rate and the reaction rate. The effectiveness factor is a function of the Thiele modulus, as a measure of how far the reactant diffuses into the catalyst particle before reacting. The value range of the effectiveness factor is from 0 to 1. As the number approaches to 1, it indicates that the internal mass transfer is negligible.

Detailed parameters used for calculating the effectiveness factor and results are summarized in Table 30.

D _e , m ² /s	8.3E-10
k_{HYD} , s ⁻¹	$1.4E-04^{a}$
Ø1	0.015
η	1

Table 30. Parameter values for estimating η .

^a average AMS hydrogenation rates at 200°C, Table 20

Since the effectiveness factor was equal to 1, the internal mass transfer was excluded.

Appendix C Carbon balance

The carbon balance of each experiment should be 100% under ideal conditions. However, due to experimental errors and analytic limitations, the carbon balance was studied for both styrene and AMS reactions. At the end of the reaction, about 15 mL solutions were lost due to GC-MS analysis (~1-2 mL) and washing the sampling line (~12-13 mL) during reaction. The carbon balance was roughly calculated based on GC-MS results. Table 31 reports the carbon recovery at 70 minutes (hydrogenation kinetic analysis region). The relatively low carbon balance in styrene reaction was observed duo to the large amount of gum formed during reaction.

Experimental #	Carbon recovery (mol %)
Styrene	82±6.6
AMS	90±7.2

Table 31. Carbon recovery summary for styrene and AMS experiments

Appendix D Experimental error analysis

The experimental reproducibility was determined by two separate AMS experiments. The RSD results of two AMS experiment conversions are shown in Table 32.

catalyst.				
Experimental #	Xu20141108	Xu20141117	RSD	
AMS Conversion, mol%	65.7	62.1	2.76%	
Cumene, mol/cm ³	1.86E-04	1.90E-04	1.08%	
AMS, mol/cm ³	1.55E-05	9.48E-07	88.5%	

Table 32. The RSD result of two AMS experiments at T=200 °C, 4.2 wt% AMS diluted in decalin, 0.2 g

Appendix E ANOVA analysis

ANOVA analysis was used to check the orthogonal analysis and to verify the styrene and AMS hydrogenation kinetic model. The α (single factor) was set at 0.1 for orthogonal analysis, in other words, the 90% confidence level, while the α was set at 0.05 for kinetics.

In ANOVA analysis, SSA and SSE are defined as the sum of squares between groups and within groups, respectively. The sum of SSA and SSE is the total sum of squares between groups (SST):

$$SST = SSA + SSE$$

Equation 28

Each of the term in the Equation 28 is defined as:

For orthogonal analysis,

$SST = \sum_{oo=1}^{9} (X_{oo} - \overline{\overline{X}})^2$	Equation 29a
SSE = SST - SSA	Equation 30a
$SSA = \sum_{i=1}^{f} n_i (\overline{T_i} - \overline{\overline{X}})^2$	Equation 31a

Note: The X_{oo} are the experimental values of orthogonal analysis. $\overline{\overline{X}}$ is the average of all

values from orthogonal analysis. $\overline{T_1}$ refers to the average of experimental values obtained from the 1st level at f variable. Besides, two freedoms are defined as d_{f1} and d_{f2} that are equal to 2 due to three three-level factor orthogonal design that was used in styrene reactions, to find the F value in the F-distribution table. Then the mean square values MSA and MSE can be calculated by Equations 32a-33a:

$$MSE = \frac{SSE}{2}$$
Equation 32a
$$MSA = \frac{SSA}{2}$$
Equation 33a

For single variable test,

$$SST = \sum_{j=1}^{k} \sum_{i=1}^{n} (X_{ij} - \overline{X})$$
Equation 29b

$$SSE = \sum_{i=1}^{k} \sum_{j=1}^{n} (X_{ij} - \overline{X}_{i})^{2}$$
Equation 30b

$$SSA = \sum_{i=1}^{k} n_{i} (\overline{X_{i}} - \overline{\overline{X}})^{2}$$
Equation 31b

Note: When i=1, the X_{1j} are the experimental concentration values. When i=2, the X_{2j} are the calculated values from the proposed kinetic model. \overline{X} is the average of all values. Besides, two freedoms are defined as d_{f1} and d_{f2} that are equal to k-1 and n-k, respectively, to find the F value in the F-distribution table. Then the mean square values MSA and MSE can be calculated by Equations 32b-33b:

$$MSE = \frac{SSE}{n-k}$$
Equation 32b
$$MSA = \frac{SSA}{k-1}$$
Equation 33b

The F value from experiment is then obtained by MSA/MSE. Two examples of ANOVA analysis for orthogonal analysis and single variable test are shown as follows:

 Table 33. An example of ANOVA analysis for styrene hydrogenation orthogonal analysis of styrene

concentration.

Source of Variation	SS	df	MS	F _{ANOVA}	F _{critical}
Between	3.09E-08	2	1.55E-08		
Within	1.58E-09	2	7.91E-10	19.54	9
SST	4.51E-08	8			

Table 34. An example of ANOVA analysis for AMS reaction at T=225 °C, 6.3 wt%AMS diluted in decalin,

0.2	g	catalyst.
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Source of Variation	SS	df	MS	F _{ANOVA}	F _{critical}
Between	1.06E-09	1	1.06E-09		
Within	5.00E-08	10	5.00E-10	0.21	4.96
SST	5.11E-08	11		-	