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In the name of Allah, the Most Gracious and the Most Merciful

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TABLE OF CONTENTS

Acknowledgments	ii
Table of contents	iii
List of tables	viii
List of figures	x
List of plates	xiii
List of abbreviations	xiv
List of symbols	xv
Abstrak	xvii
Abstract	xix

CHAPTER 1- INTRODUCTION

1.1	Air pollution	1
1.2	Automotive and industrial sector	1
1.3	Gasoline engine versus diesel engine	4
1.4	Nitrogen oxides (NO _x)	6
1.5	Problem statement	8
1.6	Objectives	9
1.7	Scope of the study	10
1.8	Organization of the thesis	10

CHAPTER 2- LITERATURE REVIEW

2.1	Introduction	13
2.2	Selective catalytic reduction (SCR) of NO _x	13
2.2.1	Mechanism of HC-SCR	16
2.2.2	Catalyst for SCR	17
2.2.2 (a)	Oxide based catalyst	17
2.2.2 (b)	Zeolite catalyst	18
2.2.2 (c)	Noble metal catalyst	18
2.2.2 (d)	Bimetallic catalyst	19
2.3	ZSM-5 as a zeolite catalyst support	20
2.3.1	ZSM-5 based catalyst	24

2.3.2	Zinc as second active metal	25
2.4	Catalyst preparation	26
2.4.1	Impregnation method	27
2.4.2	Ion-exchange method	28
2.5	Structured catalyst	29
2.5.1	Monolithic catalyst	29
2.5.2	Monolithic catalyst for SCR of NO _x	32
2.5.3	Ceramic monolithic catalyst	33
2.5.4	Washcoating method	34
2.6	Influence of gas composition on SCR of NO _x	35
2.6.1	Oxygen (O ₂)	35
2.6.2	Hydrocarbon (HC)	36
2.6.3	Nitrogen oxide (NO)	37
2.7	Optimization studies	37
2.7.1	Response surface methodology (RSM)	37
2.7.2	Central composite design (CCD)	38
2.7.3	Data analysis	39
2.7.4	Model fitting and validation	40
2.8	Catalyst characterization	40
2.8.1	Microscopy	41
2.8.2	X-ray diffraction (XRD) crystallography	41
2.8.3	Surface area, pore size distribution and adsorption-desorption isotherm	42
2.8.4	Catalyst acidity	45
2.8.5	Washcoating adherence	46
2.9	Kinetic study	46

CHAPTER 3- MATERIALS AND EXPERIMENTAL METHODS

3.1	Materials and chemicals	48
3.1.1	Catalyst	48
3.1.2	Synthetic diesel exhausts gas	49
3.2	Catalyst preparation	50
3.2.1	Zeolite modification	51

3.2.2	Metals incorporation into the catalyst	51
3.2.2 (a)	Impregnation method	52
3.2.2 (b)	Ion-exchange method	53
3.2.2 (c)	Combine method (impregnation and ion-exchange)	53
3.2.3	Catalyst particle size preparation	55
3.2.4	Preparation of washcoated monolithic catalyst	55
3.3	Experimental set up	56
3.3.1	Synthetic diesel exhaust preparation and gas flow system	57
3.3.2	Catalytic reactor	59
3.3.2 (a)	Packed bed (granular)	59
3.3.2 (b)	Monolithic catalyst	60
3.4	Catalyst characterization	60
3.4.1	Scanning electron microscopy (SEM)	60
3.4.2	X-ray diffraction (XRD)	61
3.4.3	Nitrogen adsorption	61
3.4.4	Fourier transformed infra red (FTIR) spectroscopy	62
3.4.5	Washcoating adherence	62
3.5	Catalyst activity measurement	63
3.5.1	Gas analysis system	63
3.6	SCR of NO using granular catalyst	64
3.6.1	Effect of method of catalyst preparation	65
3.6.2	Effect of metals loading	65
3.6.3	Effect of weight hourly space velocity (WHSV)	65
3.7	Design of experiment (DOE)	65
3.8	SCR of NO using ceramic monolithic catalyst study	68
3.8.1	Stability study	69
3.8.2	Kinetic study	69

CHAPTER 4- RESULTS AND DISCUSSION

4.1	Introduction	72
4.2	Catalyst characterization	73
4.2.1	Crystallinity by X-ray diffraction (XRD)	74
4.2.1(a)	XRD pattern of catalyst with different method preparation	74

4.2.1(b)	XRD pattern of catalyst with different Cu and Zn loadings	76
4.2.2	N ₂ adsorption-desorption analysis	78
4.2.2 (a)	Effect of metal incorporation methods on pore volume and pore size distribution	78
4.2.2 (b)	Effect of preparation method on pore volume and pore size distribution.	81
4.2.2 (c)	Effect of metals loading onto the catalyst on pore volume and pore size distribution	82
4.2.3	Morphology analysis	86
4.2.4	FTIR-pyridine adsorption analysis	87
4.3	Catalytic activity	89
4.3.1	Blank experiments	89
4.3.2	Reproducibility of experimental data	89
4.3.3	Effect of operating parameters on catalyst preparation	90
4.3.3(a)	Effect of preparation method of catalysts	90
4.3.3(b)	Effect of metals loading on the catalyst	94
4.3.3(c)	Effect of weight hourly space velocity (WHSV).	96
4.4	Optimization study using central composite design on catalytic activity condition	99
4.4.1	Regression Models	100
4.4.2	Adequacy of the Model	101
4.4.3	Effects of Process Variables	103
4.4.4	Optimization Analysis	106
4.5	Selective catalytic reduction (SCR) of NO in ceramic monolithic catalyst	108
4.5.1	Characterization study	108
4.5.1(a)	Catalyst concentration in the slurry	108
4.5.1(b)	Multiple depositions	110
4.5.2	Catalytic study	112
4.5.2(a)	Optimal loading of catalyst powder	112
4.5.2(b)	Stability of the washcoated ceramic monolith	114
4.5.3	Kinetic study	115

CHAPTER 5- CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	119
5.2 Recommendations	121
REFERENCES	122
APPENDICES	134
Appendix A: Calculation of weight hourly space velocity (WHSV) for powdered catalyst activity	
Appendix B: Calculation of feed gas composition and flow rates in catalytic activity test	
Appendix C: Calculation of reproducibility of data experiment	
Appendix D: Ceramic monolith catalyst	
Appendix E : Kinetic study	
LIST OF AWARD	

LIST OF TABLES		Page
Table 1.1	Total numbers of registered vehicles in Malaysia from 1998 to 2006 (Road Transport Department Malaysia, 2007)	2
Table 1.2	Air emission reduction targets for the EU (Erisman <i>et al.</i> , 2003)	3
Table 1.3	The features of gasoline engine and diesel (ISUZU, 2008)	4
Table 1.4	The environmental and health effects of NO _x (Effects of Nitrogen Oxides, 2007)	6
Table 2.1	Schematic overview of reaction mechanisms in HC-SCR	17
Table 2.2	Performance of ZSM-5 based catalyst tested for NO _x reduction	24
Table 2.3	Performance of bimetallic catalyst tested for NO _x reduction	26
Table 2.4	Performance of monolithic catalyst for SCR of NO _x	33
Table 3.1	List of materials used as the support and the structured substrate	49
Table 3.2	List of chemicals used	50
Table 3.3	Catalyst and preparation methods	52
Table 3.4	List of equipment used in catalysts preparation	55
Table 3.5	Retention times of component gases obtained using the molecular Sieve 5A columns	64
Table 3.6	Independent variables: coded and real values in central composite design	67
Table 3.7	Central composite design matrix of NO reduction process	68
Table 3.8	The space time data in the structured catalytic reactor	70
Table 4.1	Physical characteristics of metal loaded ZSM-5 based catalysts prepared through different methods	80
Table 4.2	Physical characteristics of different metal loaded ZSM5 based catalysts prepared using IMP/IE method	85

Table 4.3	Experimental data of the response in Central Composite Design (CCD)	100
Table 4.4	Analysis of variance (ANOVA) for 2 ³ full CCD design for NO reduction	103
Table 4.5	Constraint used to obtain the optimum value for NO concentration, i-C ₄ H ₁₀ concentration and reaction temperature	107
Table 4.6	Selected conditions found by DOE	107
Table 4.7	Results of verification experiments conducted at optimum conditions as obtained from DOE	108
Table 4.8	Catalyst loading and weight loss for different repeated dipping processes	110
Table 4.9	Rate constant, <i>k</i> obtained using Polymath at various temperatures	116

LIST OF FIGURES		Page
Figure 1.1	Sources of air pollution in Malaysia (Department of the Environment Malaysia, 1996)	2
Figure 1.2	Composition emissions from gasoline engine and diesel engine (McDonald, J., 2005)	5
Figure 2.1	Maximum performances for SCR of NO _x (Heck, 1999)	15
Figure 2.2	Three major families of SCR catalyst (Heck <i>et al.</i> , 1999)	18
Figure 2.3	SiO ₄ and AlO ₄ units linked through shared oxygen (Guth and Kessler, 1999).	21
Figure 2.4	Framework structure of ZSM-5 (Weitkamp, 2000)	23
Figure 2.5	Monolith channels in a cross section of 400 cells per square inch (cpsi) cordierite monolith (van Gulijk <i>et al.</i> , 2005)	30
Figure 2.6	Schematic representation of a honeycomb monolith catalyst (Vesna, 2006)	32
Figure 2.7	The IUPAC classification of adsorption isotherm shapes (Sing <i>et al.</i> , 1985)	44
Figure 2.8	The IUPAC classification of hysteresis loops (Sing <i>et al.</i> , 1985)	44
Figure 3.1	The bimetallic catalyst preparation process flow	54
Figure 3.2	Experimental set up for catalytic activity test	58
Figure 3.3	Schematic diagrams showing the arrangement of granular catalyst in reactor, structured catalyst in side view of the reactor and structured catalyst in cross sectional view of the reactor	59
Figure 4.1	XRD patterns of (a) H-ZSM-5 and Cu/Zn/ZSM-5 catalysts with different preparation methods (b) Cu/ZSM-5 (IE) (c) Cu/Zn/ZSM-5 (IE/IE) (d) Cu/Zn/ZSM-5 (IE/IMP) (e) Cu/ZSM-5 (IMP) (f) Cu/Zn/ZSM-5 (IMP/IMP) (g) Cu/Zn/ZSM-5 (IMP/IE)	75
Figure 4.2	XRD patterns of H-ZSM-5 and Cu/Zn/ZSM-5 (IMP/IE) with different Cu loadings and fixed Zn loading (1 time exchange = 8 wt. %)	77

Figure 4.3	XRD patterns of H-ZSM-5 and Cu/Zn/ZSM-5 (IMP/IE) with different numbers of Zn exchange step and fixed Cu loading (6 wt. %)	77
Figure 4.4	Adsorption/desorption isotherms of support, monometallic and bimetallic catalysts	79
Figure 4.5	Adsorption/desorption isotherms of bimetallic catalyst (Cu/Zn/ZSM-5) obtained through different preparation methods	82
Figure 4.6	Adsorption/desorption isotherms for Cu/Zn/ZSM-5 (IMP/IE) with different Cu loadings and a fixed Zn loading (8 wt. %)	84
Figure 4.7	Adsorption/desorption isotherms for Cu/Zn/ZSM-5 (IMP/IE) with different Zn loadings and a fixed Cu loading (6 wt. %)	84
Figure 4.8	Scanning electron micrographs of catalysts	86
Figure 4.9	FTIR spectra of pyridine adsorption on the H-ZSM-5 and Cu/Zn/ ZSM-5 catalysts	88
Figure 4.10	NO conversion profiles of catalysts based on different preparation methods	91
Figure 4.11	NO conversion profiles of bimetallic catalyst as compared with the monometallic catalysts	93
Figure 4.12	Effect of copper content in the $Cu_x/Zn_8/ZSM-5$ (IMP/IE) catalysts on the reduction of NO at 350°C	95
Figure 4.13	Effect of zinc content in the $Cu_6/Zn_x/ZSM-5$ catalysts on the reduction of NO at 350°C	96
Figure 4.14	NO reduction profile in the temperature range of 300-400°C at various WHSV (5,000 h^{-1} - 20,000 h^{-1}) over $Cu_6/Zn_8/ZSM-5$ (IMP/IE) catalyst	97
Figure 4.15	Catalytic activity for NO-SCR with $i-C_4H_{10}$ over Cu/Zn/ZSM-5 (IMP/IE). Reaction conditions: 1000 ppm NO, 1500 ppm $i-C_4H_{10}$, 3 v% O_2 , N_2 balance and WHSV= 13,000 h^{-1}	98
Figure 4.16	Predicted vs. actual data for % NO conversion obtained from the model	102
Figure 4.17	One factor plot of the effect of process variables: (a) temperature, (b) NO concentration and (c) $i-C_4H_{10}$ concentration on the % NO conversion	105

Figure 4.18	Interaction plots of the effect of $i\text{-C}_4\text{H}_{10}$ concentration and temperature on % NO conversion. NO concentration is constant at the zero level 1450 ppm	106
Figure 4.19	Morphology of cross sectional view of ceramic monolith catalyst	109
Figure 4.20	Morphology of the wall of the ceramic monolith catalyst seen under SEM	111
Figure 4.21	NO conversion profiles of monolith catalysts prepared with different numbers of immersions	112
Figure 4.22	Stability of Cu/Zn/ZSM-5 (IMP/IE)-washcoated ceramic monolith catalyst	115
Figure 4.23	Concentration of NO in the outlet as a function of space time at different temperatures	116
Figure 4.24	Arhenius plot for determining activation energy (E_a)	118
Figure 4.25	Comparison of simulated and experimental data of NO conversion at different temperatures	118

LIST OF PLATES

Page

Plate 3.1	Ceramic monolith substrate	49
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LIST OF ABBREVIATIONS

Analysis of variance	ANOVA
Arbitrary unit	a.u
Barret-Joyner-Halenda	BJH
Brounar-Emmett-Teller	BET
Central Composite Design	CCD
Design of Experiment	DOE
European Union	EU
Fourier transformed infra red	FTIR
Gas chromatography	GC
Gas hourly space velocity	GHSV
Hydrocarbon	HC
Hydrocarbon selective catalytic reduction	HC-SCR
Impregnation	IMP
International Union of Pure and Applied Chemistry	IUPAC
Ion-exchange	IE
Nitrogen oxides	NO _x
NO _x storage and reduction	NSR
Particulate matters	PM
Parts per million	ppm
Response surface methodology	RSM
Road Transport Department	RTD
Scanning electron microscopy	SEM
Selective catalytic reduction	SCR
Thermal conductivity detector	TCD
Three-way catalyst system	TWC
Volatile organic compound	VOC
Weight hourly space velocity	WHSV
X-ray diffraction	XRD
Zeolite socony mobil 5	ZSM-5

LIST OF SYMBOLS

Symbols	Description	Unit
A	Arrhenius factor	Dimensionless
a, b, c	Reaction order	Dimensionless
$(C_{NO})_{in}$	Inlet concentration of nitrogen oxide	[ppm]
$(C_{NO})_{out}$	Outlet concentration of nitrogen oxide	[ppm]
$(C_{HC})_{in}$	Inlet concentration of hydrocarbon	[ppm]
$(C_{HC})_{out}$	Outlet concentration of hydrocarbon	[ppm]
C_{NOo}	Initial concentration of nitrogen oxide	[mol/m ³]
C_{HC0}	Initial concentration of hydrocarbon	[mol/m ³]
C_{NO}	Concentration of nitrogen oxide	[mol/m ³]
C_{HC}	Concentration of hydrocarbon	[mol/m ³]
C_1	Initial concentration of the gas	[ppm]
C_2	Final concentration of the gas	[ppm]
$d C_{NO} / d \tau$	Differential of C_{NO} polynomial with respect to τ	[mol/m ³ .s]
E_a	Activation energy	[kJ/mol]
GHSV	Gas hourly space velocity	[h ⁻¹]
h	Time	[hour]
k	Reaction rate constant	[m ³ /mol.s]
M	Concentration	[molar]
P/P_o	Relative pressure	Dimensionless
R	Rate constant	[J/mol.K]
$-r_{NO}$	Rate of reaction for homogeneous model	[mol/m ³ .s]
$(-r_{NO})_{calculation}$	Rate of reaction calculated by the Polymath programme	[mol/m ³ .s]
$(-r_{NO})_{exp}$	Rate of reaction obtained from experimental data	[mol/m ³ .s]
T	Temperature	[K]
V_1	Initial gas flow rate	[ml/min]
V_2	Final gas flow rate	[ml/min]
v_o	Inlet volumetric flow rate	[ml/h]
V	Volume occupied by the catalyst bed	[ml]
wt.	Weight	[g]

w_1	Weight of coated monolith	[g]
w_2	Weight of coated monolith undergoing ultrasonic vibration	[g]
w	Weight of uncoated monolith	[g]
WHSV	Weight hourly space velocity	[h ⁻¹]
X_{NO}	Fractional conversion of NO	Dimensionless
$(X_{NO})_{\text{calculation}}$	Simulated value of fractional conversion of NO conversion	Dimensionless
$(X_{NO})_{\text{exp}}$	Experimental value of fractional conversion of NO conversion	Dimensionless
X_i and X_j	Factors (independent variables)	
Y	The response calculated by the model	
τ	Space time	[s]
α	Distance from the center of the design space to an axial point	Dimensionless
β_0	Constant coefficient	Dimensionless
B_i	Coefficients for the linear effects	Dimensionless
B_{ii}	Coefficients for the quadratics effects	Dimensionless
B_{ij}	Coefficients for the interactions effects	Dimensionless
ε	Error of quadratic model in central composite design	Dimensionless
ΔG°	Gibbs Energy	kJ/mol

MANGKIN DWI-LOGAM MONOLIT BAGI PENURUNAN BERMANGKIN NO_x TERTENTU DALAM EKZOS ENJIN DIESEL

ABSTRAK

Nitrogen oksida (NO_x) merupakan pencemar udara utama di seluruh dunia. Penurunan bermangkin NO_x tertentu dengan hidrokarbon adalah kaedah yang berpotensi dalam menyingkirkan NO_x dari ekzos diesel. Pembangunan mangkin yang dapat mengatasi kelemahan mangkin sedia ada menjadi perhatian. Mangkin yang unggul perlu menunjukkan aktiviti dan kestabilan yang tinggi serta diperbuat daripada bahan yang murah. Reaktor lapisan terpadat bermangkin lazimnya mempunyai kelemahan yang disebabkan oleh kejatuhan tekanan yang tinggi yang boleh memberi kesan kepada prestasi reaktor tersebut. Mangkin monolit mampu memberikan penyelesaiannya. Kajian ini bertujuan untuk menghasilkan mangkin monolit yang diperbuat daripada bahan yang murah serta boleh membangunkan prestasi penurunan bermangkin NO_x tertentu ke tahap yang lebih tinggi.

Mangkin dwi-logam (Cu/Zn/ZSM-5) telah dibangunkan dengan menggabungkan kuprum (Cu) dan zink (Zn) berserta zeolit ZSM-5 (Si/Al=40) sama ada menggunakan kaedah dijerap isi (IMP) atau pertukaran ion (IE) dalam turutan kaedah yang berbeza dengan kandungan logam antara 2 dan 14 % berat. Seterusnya, mangkin dwi-logam tersebut diselaputkan ke monolit seramik yang bergaris pusat 2.0 sm dan panjangnya 6.0 sm serta mempunyai 400 sel dalam setiap inci persegi. Mangkin ini dicirikan dengan menggunakan mikroskop elektron imbasan (SEM), belauan sinar-X (XRD), analisis permukaan, spektroskop infra-merah terjelma fourier (FTIR) dan rawatan ultrabunyi untuk menguji ketahanan selaput mangkin yang diselaputkan ke monolit seramik. Aktiviti kajian ini telah dijalankan menggunakan reaktor kaca yang bergaris pusat dalam 15 mm dan 25.4 mm masing-

masing untuk mangkin berserbuk dan berstruktur. Aktiviti ini juga beroperasi antara 200 dan 550 °C serta halaju ruang jaman gas (GHSV) ialah 13,000 per jam. Campuran gas yang digunakan ialah 1000 ppm NO, 1500 ppm iso-butana (i-C₄H₁₀), 3 % isipadu O₂ dan selebihnya adalah N₂. Rekabentuk eksperimen (DOE) dengan 3 parameter digunakan dengan kepekatan NO dan i-C₄H₁₀ adalah di antara 900 dan 2000 ppm serta suhu di antara 300 dan 400 °C.

Berdasarkan prestasi pemangkinan dan pencirian mangkin yang telah dijalankan, kaedah penggabungan logam terbaik ialah dengan menjerap isi logam kuprum dan menukar ion logam zink sementara kandungan logam optima ialah masing-masing 6 % berat dan 8 % berat untuk kuprum dan zink. Keadaan operasi terbaik yang diperoleh menerusi kajian DOE adalah dengan menggunakan campuran gas yang mengandungi NO berkepekatan 900 ppm, i-C₄H₁₀ berkepekatan 2000 ppm, 3 % isipadu O₂ dan selebihnya adalah N₂ sebagai gas masukan. Kaedah ini memberi keputusan ~90 % penurunan NO_x antara 300 dan 400 °C untuk mangkin Cu/Zn/ZSM-5 berserbuk. 1.8 g mangkin pada monolit seramik diperoleh dengan menyelaput Cu/Zn/ZSM-5(IMP/IE) dengan 6 % berat Cu dan 8 % berat Zn sebanyak 2 kali dapat menurunkan NO_x sebanyak ~88 % apabila dijalankan dalam keadaan operasi yang sama. Selain menunjukkan aktiviti pemangkinan yang tinggi, mangkin monolit juga stabil sehingga 72 jam dengan penurunan aktiviti hanya 10 %. Tenaga pengaktifan yang rendah iaitu +30.30 kJ/mol turut diperoleh daripada tindak balas tersebut.

Kesimpulannya, mangkin Cu/Zn/ZSM-5 (IMP/IE) dengan 6 % berat Cu dan 8 % berat Zn yang diselaputkan ke monolit seramik merupakan mangkin yang praktikal dan ekonomik untuk penurunan NO_x berdasarkan kepada kos bahan yang murah disamping memberikan prestasi pemangkinan yang tinggi.

BIMETALLIC MONOLITHIC CATALYST FOR SELECTIVE CATALYTIC REDUCTION OF NO_x IN DIESEL ENGINE EXHAUST

ABSTRACT

Nitrogen oxides (NO_x) are major air pollutants worldwide. Selective catalytic reduction (SCR) of NO_x by hydrocarbons is a potential method for removing NO_x from diesel exhaust. The development of a suitable catalyst which could circumvent the drawbacks of the existing catalyst is an area of considerable interest. An ideal catalyst should show high activity, high stability and made up of low cost materials. A packed bed catalytic reactor usually subjects to a drawback of high pressure drop that affects its performance and monolithic catalysts provide a plausible solution. Thus, this study was dedicated to the use of low cost material in developing high performance monolithic catalyst for SCR of NO_x.

In this study, a bimetallic catalyst (Cu/Zn/ZSM-5) was developed by incorporating copper (Cu) and zinc (Zn) onto ZSM-5 zeolite (Si/Al=40) using either impregnation (IMP) or ion exchange (IE) method in different orders with metal loadings range between 2 wt. % and 14 wt. %. Then, the bimetallic catalyst was washcoated onto a 400 cell per square inch (cps) ceramic monolith with a diameter of 2.0 cm and a length of 6.0 cm. The catalyst were characterized using scanning electron microscope (SEM), X-ray diffraction (XRD), surface analysis, fourier transformed infra red (FTIR) spectroscopy and ultrasound treatment for washcoating adherence of catalyst coating onto the ceramic monolith. The activity study was performed in a glass reactor 15 mm and 25.4 mm internal diameter for powdered and structured catalyst, respectively. It was operated between 200 °C and 550 °C of 13,000 h⁻¹ of gas hourly space velocity (GHSV) with the gas mixture of 1000 ppm of NO, 1500 ppm of iso-butane (i-C₄H₁₀), 3 v/v % of O₂ and N₂ as the balance. The

Design of Experiment (DOE) with 3 parameters was studied whereby the NO and i-C₄H₁₀ concentration are between 900 and 2000 ppm and the temperature between 300 °C and 400 °C.

Based on the catalytic performance and characterization study, the best metal incorporation methods were by impregnating the Cu and ion exchanging the Zn while the optimum metals loadings were 6 wt. % and 8 wt. % of Cu and Zn, respectively. The best operating conditions were obtained from DOE study whereby a mixture of 900 ppm of NO, 2000 ppm of i-C₄H₁₀, 3 v/v % of O₂ and N₂ as the balance as the inlet gas should be used to result in ~90 % of NO_x reduction for powdered Cu/Zn/ZSM-5 catalyst at between 300 °C and 400 °C. 1.8 g of Cu/Zn/ZSM-5 (IMP/IE) catalyst with 6 wt. % of Cu and 8 wt. % of Zn obtained by 2 times of washcoating step onto the ceramic monolith showed ~88 % of NO_x reduction in the same operating conditions. Besides showing high catalytic activity, the monolithic catalyst was also stable for up to 72 h with an activity drop of only 10 %. Furthermore, low activation energy of +30.30 kJ/mol was obtained for the reaction.

As a conclusion, the Cu/Zn/ZSM-5 (IMP/IE) catalyst with 6 wt. % of Cu and 8 wt. % of Zn washcoated onto the ceramic monolith was an economic catalyst for the NO_x reduction due to the relatively low cost materials used and at the same time, demonstrating high catalytic performance.

CHAPTER 1

INTRODUCTION

1.1 Air pollution

Air pollution is a phenomenon where chemical, physical or biological agent modifies the natural characteristics of the atmosphere. The types of pollutants are particulate matter and noxious gases such as sulfur dioxide, carbon monoxide, nitrogen oxides, and chemical vapors. Worldwide air pollution is responsible for large numbers of health problems and cases of respiratory.

The three major sources of air pollution in Malaysia are mobile sources, namely vehicles, stationary sources such as factories and open burning of municipal and industrial wastes, whereby contributing to at least 70–75 %, 20–25 % and 3–5 %, respectively (Afroz *et al.*, 2003). According to the Department of the Environment (DOE, 1996), Malaysia, in 1996, the percentages, of the air emission load by type were motor vehicles, 82 %; power stations, 9 %; industrial fuel burning, 5 %; industrial production processes, 3 %; domestic and commercial furnaces, 0.2 %; and open burning at solid waste disposal sites, 0.8 % as shown in Figure 1.1. Mostly, these sources contribute to the air pollution through the combustion of fossil fuels to meet the society requirements of energy.

1.2 Automotive and industrial sector

Movement of people and goods requires energy which relies mostly on the burning of fossil fuels. Statistics from the Road Transport Department (RTD), Malaysia as shown in Table 1.1 indicate that the total number of registered vehicles in Malaysia increase every year from 420,464 (in 1998) to 1,939,234 (in 2006) (Road

Transport Department, Malaysia, 2007). The year 2000 saw over 500 million passenger cars in use worldwide with an annual worldwide production of new cars approaching 60 million. The demand for transportation is growing fast due to highly dependence of modern society on motorized transportation such as cars, trucks, and railways.

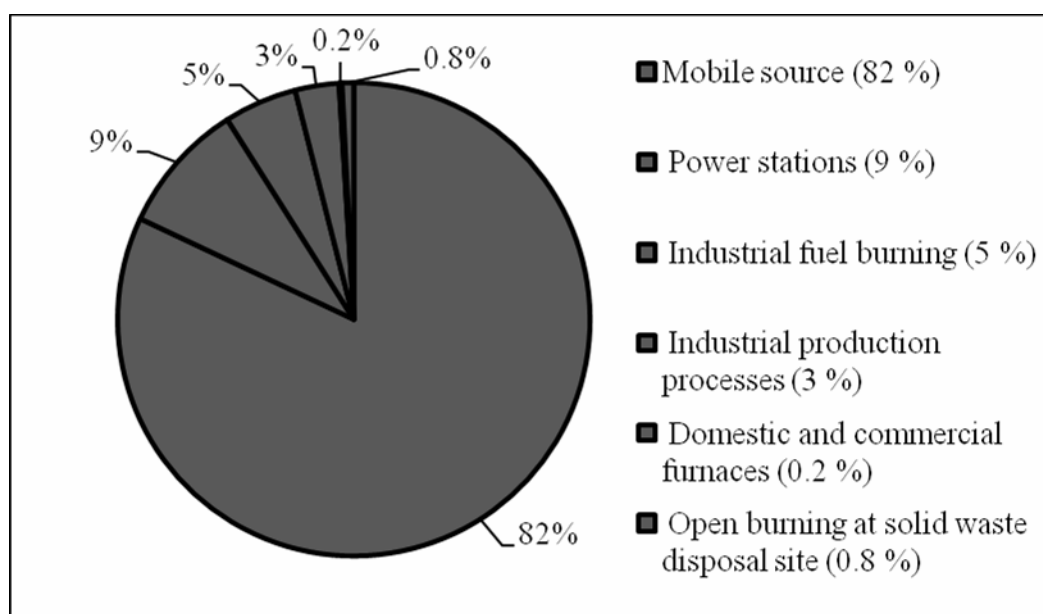


Figure 1.1: Sources of air pollution in Malaysia (Department of the Environment Malaysia, 1996)

Table 1.1: Total number of registered vehicles in Malaysia from 1998 to 2006 (Road Transport Department Malaysia, 2007)

Year	Number of registered vehicles
1998	420, 464
1999	565, 741
2000	625, 869
2001	675, 289
2002	691, 188
2003	800, 790
2004	932, 363
2005	1, 020, 108
2006	1, 939, 234

The goal of achieving developed country status corresponding by the year 2020 results in the growing number of industries in Malaysia whereby the increase in the energy is expected. In 2000, the industrial sector consumed 37.1 % of the total fuel consumption and the demand is growing at a rate of 8.5 % annually (The Sun, 2003).

The modern and developed life is not the excuse to neglect the environment. Legal limits for emissions in exhaust gases either from mobile or stationary sources are still becoming stricter. Emission standards for heavy duty vehicles in 2007 and beyond will require a 90 % reduction in total emission from 2003 levels (U.S EPA, 2001). Each government has its own standards for air contaminants. These standards are maximum concentrations, which may be present in air. The standards may vary greatly between various countries. Governments of different countries, for example in the European Union, trying to suit their policies for air contamination standards as shown in Table 1.2.

Table 1.2: Air emission reduction targets for the EU (Erisman *et al.*, 2003)

Policy/ Pollutant	Base year	Target year	Reduction (%)
<i>5th Environmental Plan</i>			
Sulphur dioxide	1985	2000	35
Nitrogen dioxide	1990	2000	30
<i>Dir. on Nat. Emission ceiling (NECD)^c</i>			
Sulphur dioxide	1990	2010	78
Nitrogen dioxide	1990	2010	55

^cTargets from first NOx protocol

These standards and at the same time, a strong pressure to lower the fuel consumption for economic purposes and to lower the production of carbon dioxide, which is an important greenhouse gas create the demand for more efficient engines.

1.3 Gasoline engine versus diesel engine

The diesel engines seem to be the alternative to the gasoline engines. Diesel engines are run under oxygen excess condition a so called lean-burn operation. The features of gasoline engine and diesel engine are shown in Table 1.3. Since diesel engines have a high thermal efficiency than gasoline engines, they have lower fuel consumption (20-40 % lower than gasoline engines), consequently, the amounts of carbon dioxide (CO₂), carbon monoxide (CO) and hydrocarbon (HC) emitted are also low (Amberntsson *et al.*, 2001).

Table 1.3: The features of gasoline engine and diesel (ISUZU, 2008)

	Gasoline Engine	Diesel Engine
Combustion process	Air and fuel are mixed in advance and then drawn into the cylinder and compressed. The compressed mixture is ignited by an ignition plug.	Air is drawn into the cylinder and highly compressed. Then, fuel is sprayed into the cylinder under high pressure. Ignition occurs spontaneously as a result of the high temperature generated through compression.
Thermal Efficiency (Ratio of heat converted into power against total heat generated during combustion)	25-30%	35-42%

Currently, the diesel engine owes its popularity to its high fuel efficiency, reliability, durability and relatively low fuel price. In UK and the rest of Europe, the

proportion of passenger cars fuelled by diesel is increasing. Specifically in the UK, the proportion is expected to reach 40 % in 2010 compared with only 12 % in 2000. (Carslaw *et al.*, 2005). Furthermore, diesel engines also achieved a growing share of the light-duty vehicle market with 60% of all commercial vans are currently equipped with this engine (Fino, 2007).

However, the operation of the lean-engine increases the production of toxic gas e.g nitrogen oxides (NO_x) compared to gasoline engines as shown in Figure 1.2. The high temperatures that occur in the combustion chamber promote an unwanted reaction between nitrogen and oxygen from the air. This result in various oxides of nitrogen, commonly called NO_x (Fuel News Diesel Engine Emissions, 2002).

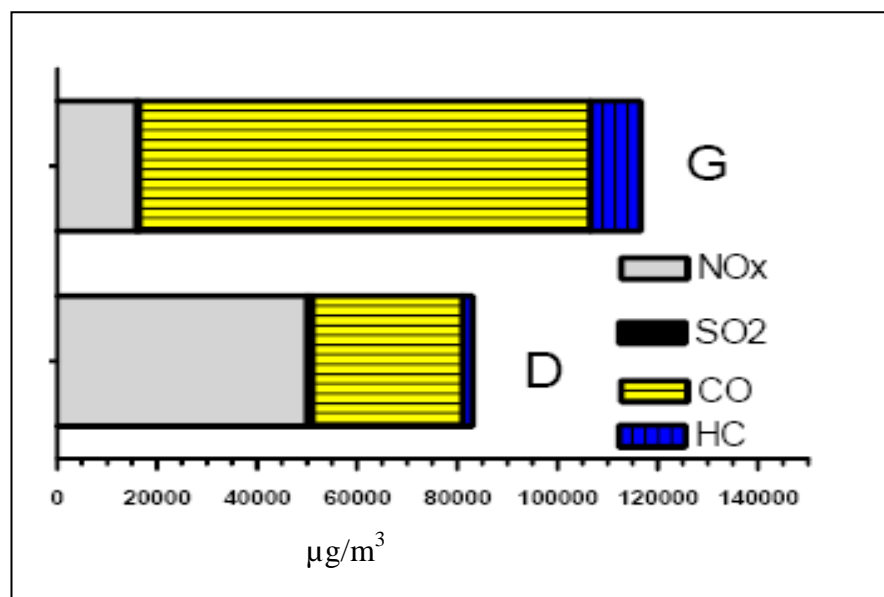


Figure 1.2: Composition emission from gasoline engine (G) and diesel engine (D) (McDonald, J., 2005)

1.4 Nitrogen oxides (NO_x)

In atmospheric chemistry, the term nitrogen oxides or “NO_x” is used to refer to the total concentration of nitrogen monoxide (NO), nitrogen dioxide (NO₂) and nitrous oxide (N₂O) which is important air pollutants produced from combustion processes. NO_x are highly reactive gases that contain nitrogen and oxygen in varying amounts. Many of the nitrogen oxides are colorless and odorless. However, one common pollutant, nitrogen dioxide (NO₂) along with particles in the air can often be seen as a reddish-brown layer over many urban areas.

NO_x has a direct impact on environment and human. It is due to the formation of irritating ground level ozone and its reaction with other chemicals present in the air to form toxic chemicals, nitrate particles and acid aerosols. Table 1.4 summarizes the environmental and health effects of NO_x.

Table 1.4: The environmental and health effects of NO_x (Effects of Nitrogen Oxides, 2007)

Environmental effects	Health effects
<ul style="list-style-type: none">• Combines with other pollutants to form ozone and acid rain that harms vegetation and ecosystems.• Acid rain causes deterioration of cars, buildings and historical monuments and causes lakes and streams to become acidic and unsuitable for many fish.• Contributes to nutrient overload that impairs water quality, leads to oxygen depletion and reduces fish and shellfish populations• Contributes to global warming	<ul style="list-style-type: none">• Associated with respiratory problems• Can aggravate existing respiratory conditions (asthma and bronchitis)• Damages lung tissue and reduces lung function• Premature death (particles)

The emission of NO_x is regulated differently in the various industrialized countries. In Malaysia, emissions of smoke and gaseous pollutants such as carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NO_x) and particulate matters (PM) from motor vehicle exhausts are controlled under the Environmental Quality (Control of Emission from Diesel Engines) Regulations 1996 and the Environmental Quality (Control of Emission from Petrol Engines) Regulations 1996. NO_x emissions are still 37 % higher than the target fixed for 2010 by the Gothenburg protocol. Since the control of NO_x emission is required, reduction of NO_x emission is an important issue to protect the environment.

There are many available NO_x control technologies commonly used by industry or transportation devices. They can either destroy or remove NO_x from an exhaust stream before it is emitted into the atmosphere. Among others, catalytic removal of NO_x is one of the most practical and effective methods for the abatement of NO_x emission. This is due to the decomposition of nitrogen monoxide that is thermodynamically favorable under pressures and temperatures found in diesel engine exhaust. From a thermodynamic point of view, NO and NO₂ are unstable as given in equation (1.1) and (1.2):



Despite this thermodynamic instability, kinetic studies have revealed that the activation energy for homogeneous decomposition of NO is high (~335 kJ/mol)

(Garin, 2001). Therefore, a suitable catalyst is necessary to lower this activation energy in order to facilitate this decomposition reaction.

Typical examples of catalytic removal of NO_x are the three-way catalyst system (TWC) for gasoline-fueled engines and the selective catalytic reduction (SCR) and NO_x storage and reduction (NSR) for diesel-fueled engines (Hasegawa *et al.*, 2005). Although the TWC works very well in the case of gasoline engines exhaust gases, it is not effective for NO_x reduction in oxygen-rich exhaust such as from diesel engine. Oxygen will compete with NO for adsorption sites. As a result, high reaction temperature and/or gaseous reductant are required to remove surface oxygen and regenerate catalytic activity.

Currently, the SCR is among major approaches that have reached the production stage. In the SCR, a reductant such as hydrocarbon (HC), carbon monoxide (CO), hydrogen (H₂), and ammonia (NH₃) is added to the exhaust to selectively reduce NO_x to form nitrogen and water whereby the process is catalyzed by precious metals. The typical characteristics of a SCR process includes the effectiveness of NO_x reduction can consistently reach 85 % (Orsenigo *et al.*, 1996).

1.5 Problem Statement

There have been a number of reports on SCR process. However, the main drawbacks for the successful application of the existing SCR process are limited activity due to the pressure drop that increases with decreasing catalyst particle size. Furthermore, the conventional catalysts also use high cost noble metals such as platinum (Pt), palladium (Pd) and rhodium (Rd) as the active material.

In order to overcome the existing problem, a monolithic catalyst will be produced using low cost metal species that are sufficiently active for optimum reduction of NO_x. The catalyst consists of a support with a porous washcoat containing the active material. In this study, a ceramic monolith will be used to overcome the pressure drop and it will be washcoated with zeolite which is well-known to have large specific surface area, so that the specific surface area of the catalyst can be improved. In this research, bimetallic catalyst using copper (Cu) and zinc (Zn) will be used as an active metal to improve the NO_x conversion efficiency of the catalyst and also to act as substitutes for noble metals to decrease the cost of the catalyst. An active low cost SCR monolithic catalyst with low pressure drop would be appeared to be an ideal catalyst for the de-NO_x of a diesel engine exhausts in this research.

1.6 Objectives

The present research has the following objectives:

- 1) To investigate the best method of bimetallic granular and monolithic based on Cu and Zn catalysts preparation, and the optimum metals composition of the catalysts for the SCR process.
- 2) To characterize the catalysts.
- 3) To optimize the operating conditions in NO reduction process using Design of Experiment (DOE).
- 4) To study the SCR process of monolith catalyst by implementation the optimum condition in terms of preparation, metal loading and catalytic activity parameter.

- 5) To perform the kinetic study of NO reduction process using monolithic catalyst.

1.7 Scope of the study

This research presents an investigation of the suitability of ceramic monolith catalysts in NO reduction in synthetic diesel engine exhaust using iso-butane as the reductant. Bimetallic catalysts in granular form was prepared using low cost metal (copper and zinc) and ZSM5 as the support. These catalysts were tested to check their performance in NO_x reduction. The parameters studied were the effect of preparation method using impregnation and ion-exchange method, the effect of metal loading in the catalyst and the weight hourly space velocity (WHSV). The optimum conditions such as temperature, NO_x concentration and iso-butane concentration were obtained using Design of Experiment (DOE). The best catalyst and the optimum conditions were used to study the performance of monolithic catalyst. The ceramic monolith catalyst was tested to check its performance in NO_x reduction and its stability. Besides that, a kinetic study of the reaction process using monolithic catalysts was carried out to obtain the activation energy (E), frequency factor (A) and reaction order of the reaction. The granular catalysts and ceramic monolith catalyst were characterized using SEM, XRD, ASAP micrometric and FTIR to obtain their chemical and physical properties.

1.8 Organization of the thesis

There are five chapters covered in the thesis.

Chapter 1 covers the introduction of air pollution which focuses on one pollutant (i.e NO_x) which produced from mobile source. Besides that, this chapter

also covers the introduction of NO_x in terms of definition, the health and environment significance of NO_x, regulation of NO_x emission and NO_x control technologies. The NO_x control technologies are discussed with particular focus on SCR. This chapter also presents the problem statement, objectives of the present studies, research scope and finally thesis organization.

Chapter 2 provides literature review that covers the information on the catalyst for NO_x reduction process in terms of catalyst support, active metal, catalyst preparation and metal loading composition. It also reviews on ceramic monolith catalyst followed by catalyst characterization methods such as microscopy, XRD crystallography, surface area, pore size distribution, adsorption-desorption isotherm and catalyst acidity. Besides that, this chapter also reviews on the factors that effect to SCR performance such as hydrocarbon as reducing agent, the presence of oxygen, reaction temperature and amount of catalyst in terms of weight hourly space velocity (WHSV). Finally, this chapter covers about the optimization studies in terms of Design of Experiment (DOE).

Chapter 3 presents the experimental procedures and analysis required in NO_x reduction. The first section describes the materials and chemicals used in the present study followed by second section which reveals the procedures used in the catalyst preparation. The experimental set up for NO_x reduction process is described in section three followed by catalyst characterization in section four. In section five, a catalyst activity measurement was then briefed. SCR of NO studies and optimization study using granular catalyst are described in section six and seven, respectively. Finally, the last section explains the SCR of NO studies using ceramic monolith catalyst.

Chapter 4 covers results and discussion and presents all the obtained results and provides an analysis for the findings followed by discussion. The first section covers the characterization of the synthesis granular catalysts followed by the catalytic activity of the catalyst. Then, the next section covers the Design of Experiment (DOE) to identify the optimum conditions for the SCR process. Finally, the last section covers characterization of the ceramic monolith catalyst and its catalytic activity followed the kinetic study of the reaction.

Chapter 5 summarizes the conclusions made in the present study and recommendations for future research in this particular area. The conclusions are written based on the findings reported in Chapter 4. Recommendations for future studies are presented due to their significance with the current research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

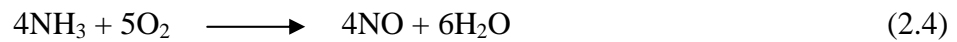
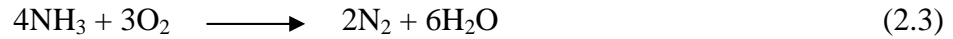
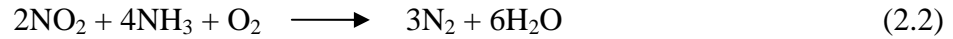
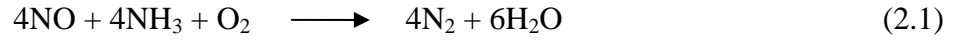
Catalysis is a key technology to provide realistic solutions to many environmental issues. Environmental catalysis refers to catalytic technologies for reducing emissions of environmentally unacceptable compounds. Problems addressed in regard to these catalytic cleanup technologies are mobile emission control, NO_x removal from stationary sources, sulfur compounds and VOC (volatile organic compound) conversion, liquid and solid waste treatment (polymers and other solid waste), and green house gas abatement or conversion.

The present study is focused on the catalytic method for reduction NO_x from diesel engine exhaust using hydrocarbons as ‘selective’ reducing agents. This process is the so-called hydrocarbon selective catalytic reduction (HC-SCR) of nitrogen oxides. This possible NO_x control technologies has attracted attention and have been reviewed in recent reports (Abu-Jrai and Tsolakis, 2007; Guzman-Vargas *et al.*, 2005; Komvokis *et al.*, 2007; Sarellas *et al.*, 2006; Satokawa *et al.*, 2007; Shichi *et al.*, 2007; Shimizu *et al.*, 2007).

2.2 Selective catalytic reductions (SCR) of NO

Selective catalytic reductions (SCR) of NO utilize a chemical reaction through catalytic modules with reducing agent to convert nitrogen oxides (NO_x), primarily NO, to nitrogen and water. The “selective” term refers to the ability of reducing agent to react selectively with NO_x instead of being oxidized by oxygen to

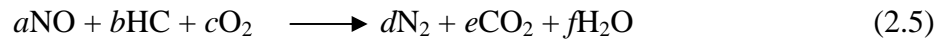
form N₂, N₂O and NO (Forzatti, 2001). The SCR of NO by ammonia is the most widespread method. The reaction involves is:



Ammonia reacts selectively to reduce the NO_x as reaction (2.1) and (2.2) while the reaction (2.3) and (2.4) are non-selective reactions which consumes the reagent and reduces the NO_x conversion.

NH₃ can be produced “on board” by thermal decomposition, for example, of urea, that must be carried in an additional tank or by the production of ammonia in a special NH₃ generator that is filled with solid ammonium carbamate (Salker and Weisweiler, 2001). Typically, stoichiometric control of the ammonia must be maintained to avoid emissions of unreacted ammonia. The advantages of NH₃ as reducing agent are its high selectivity towards reaction with NO in the presence of O₂ and the promotional promoting effect of O₂ on the rate of NO- NH₃ reaction. However, the SCR of NO by ammonia has few problems including the storage and transportation of ammonia. Furthermore, the use of NH₃-based SCR technologies is not practical for transportation applications such as the control of NO_x from diesel exhaust due to the variety of transient conditions and the complications of maintaining an on-board source of ammonia.

A new technology that has the potential to overcome these problems is the SCR of NO by hydrocarbon (HC). HC can be generated from the fuel and therefore no additional tank for its storage is required to make it suitable to apply for mobile applications. The reactions involve are;



The undesirable reaction (2.6) consumes the hydrocarbon by reaction with the O₂ present in the exhaust. This reaction is more dominant as the temperature is increased resulting in a decrease in conversion of NO_x (Heck *et al.*, 2001). Nevertheless, both reducing agents show the same characteristic which can be seen in Figure 2.1 (Heck, 1999).

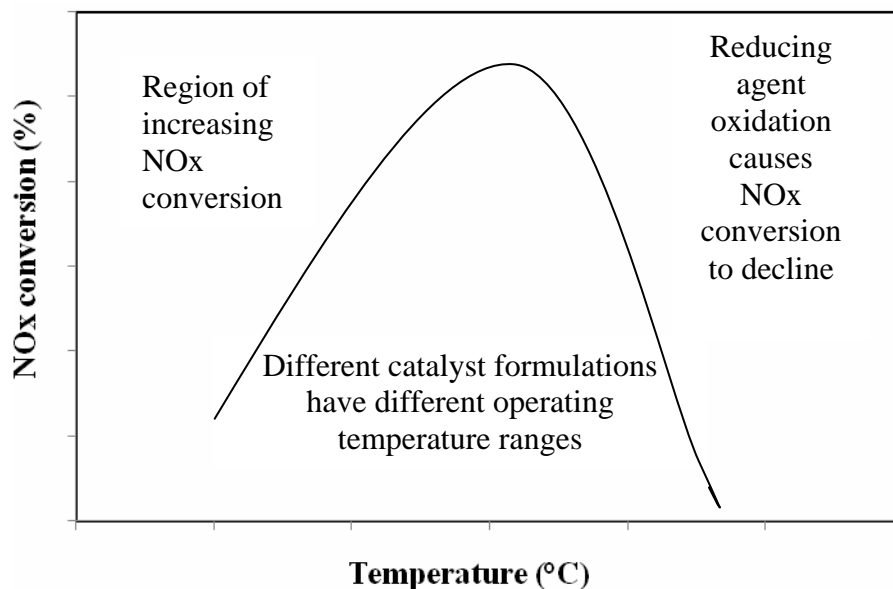


Figure 2.1: Maximum performance for SCR NO_x (Heck, 1999).

2.2.1 Mechanism of HC-SCR

Roughly, all mechanisms of HC-SCR can be divided into 3 groups as shown in Table 2.1. The first group comprises mechanisms where the catalytic decomposition of NO to N₂ and adsorbed oxygen is an important step. Thereby, the hydrocarbon serves as a scavenger which liberates the catalyst surface from adsorbed oxygen and/or to reduce the active metal. This mechanism was propagated by Inui *et al.* (1993) as their so-called microscopic sequential reaction mechanism. Burch *et al.* (1994) proposed this mechanism for C₃H₆-SCR on Pt/Al₂O₃ and could explain the formation of N₂O on Pt by the reaction of adsorbed nitrogen with adsorbed nitric oxide.

The second group includes mechanisms where the oxidation of NO to NO₂ is the vital reaction. In dependence on the reducibility of the metal, NO can be oxidized by the metal (Descorme *et al.*, 1998) and/ or by O₂ (Kikuchi *et al.*, 1996; Yan *et al.*, 1998;) on acid sites of the zeolite (Kikuchi *et al.*, 1996) or on metal sites (Miller *et al.*, 1998). The next step of the reaction sequence is then the reaction of NO₂ with the HC to N₂, possibly via organic intermediates such as nitro compounds. This reaction can also take place on acid sites of the zeolite or on metal sites.

The third group mechanisms is the hydrocarbon is partially oxidized by O₂ or NO. In the second step, the oxygen- and/ or nitrogen-containing organic intermediate such as nitro species, reacts with nitrogen oxides to N₂, CO and H₂O (Li *et al.*, 1994).

Table 2.1: Schematic overview of reaction mechanisms in HC-SCR

Catalytic decomposition of NO and subsequent regeneration of the active site by hydrocarbon.		
2 NO	\longrightarrow	$\text{N}_2 + 2 \text{ O(ads.)}$
$\text{HC} + \text{O(ads.)}$	\longrightarrow	$\text{CO}_x + \text{H}_2\text{O}$
Oxidation of NO to NO ₂ which acts as a strongly oxidizing agent		
$\text{NO} + \frac{1}{2} \text{ O}_2 \text{ or MeO}$	\longrightarrow	NO_2
$\text{NO}_2 + \text{HC}$	\longrightarrow	$\text{N}_2 + \text{CO}_x + \text{H}_2\text{O}$
Partial oxidation of the hydrocarbon		
$\text{HC} + \text{O}_2 \text{ and/or NO}_x$	\longrightarrow	HC^*
$\text{HC}^* + \text{NO}_x$	\longrightarrow	$\text{N}_2 + \text{CO}_x + \text{H}_2\text{O}$

2.2.2 Catalyst for SCR

A large number of catalysts for use in SCR were investigated and reported in the literature. The major catalyst used are oxide based catalyst, zeolite catalyst and noble metal catalyst which are active in SCR as can be proved by general performance characteristics as shown in Figure 2.2 (Heck *et al.*, 1999).

2.2.2(a) Oxide based catalyst

The V₂O₅/TiO₂ is the example of oxide based catalysts. Others oxide based catalyst which have been reported to be active in SCR are Cu/Al₂O₃ (Anderson *et al.*, 1997), Ag/ Al₂O₃ (Jen, 1998) and Pd/ ZrO₂ (Bahamonde *et al.*, 2003). However, the oxide based catalysts are not tolerance to sulfur. Miyadera. (1993) reported that although Ag/Al₂O₃ showed high activity for NO_x reduction in the presence of SO₂ but the significant decrease in the catalytic activity in the presence of SO₂ poses a problem for Ag/Al₂O₃ system.

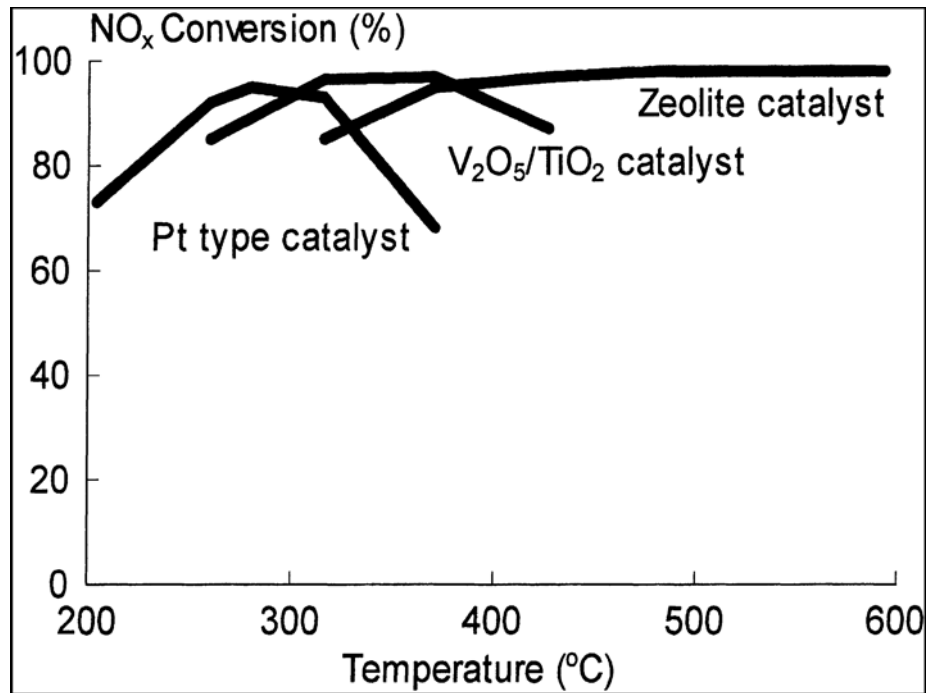


Figure 2.2: Three major families of SCR catalyst (Heck *et al.*, 1999)

2.2.2 (b) Zeolite catalyst

Zeolite catalysts are also active in SCR. Several studies on H-zeolites such as H-Mordenite and H-ZSM-5 were reported. Iwamoto *et al.* (1986) found that Cu/ZSM-5 is an active catalyst for HC-SCR. Following this finding, many catalysts using other transition metal oxides, as well as zeolite-type catalysts have been found active in this reaction such as Co/BEA (Tabata *et al.*, 1998), Ni, Cr, Fe, Mn, Ga, In with BEA (Kikuchi *et al.*, 1996). These catalysts showed high activity and durability in the presence of H₂O and SO₂ which are among the requirements for practical application as these compounds always present in the emission gases.

2.2.2(c) Noble metal catalyst

Rh/ZSM-5, Pt/ZSM-5, Pt /Al₂O₃ and Pt/SiO₂ are examples of supported noble metals catalyst studied for the SCR of NO_x. The performance of noble metal catalyst could vary from almost inactive to highly selective, a highly active but non-selective,

depending on the metal loading and the acidity of the support. Several authors have shown that when a noble metal is supported on acidic materials, such as zeolite or zirconia, it can be active and highly selective in the presence of excess oxygen (Misono *et al.*, 1997). The efficiency SCR of NO_x is only slightly affected by the presence of water (H₂O), but it is quite sensitive to sulphur dioxide poisoning (Tran *et al.*, 2008). Another problem associated with these catalysts high activity is accompanied by the formation of large concentration of N₂O, a pollutant by itself (Fritz *et al.*, 1997). Another problems with these catalysts are their high cost and that in many cases their temperature activity range is very narrow as reported by Ismail *et al.* (2002) who reported that the Pt/ZSM-5 was active in the low temperature region with maximum NO conversion of 70 % at 250 °C.

2.2.2 (d) Bimetallic catalyst

Bimetallic catalysts have created particular interest due to the promoting effect between species. The bimetallic catalyst was also introduced in the HC-SCR de-NO_x study to improve the performance of the monometallic catalysts by adding certain promoters. The second metal able to maintain first metal in the active state whereby when one of the metals is easily reduced the other stays in a low oxidation state (Guczi *et al.*, 1999; Goncalves *et al.*, 2006). The bimetallic formulation have higher resistance towards metal sintering and loss of contact between metal and support whereby in this case, the addition of a second metal can have a promoting effect leading to direct or indirect interaction of the difficulty to reduce metal with the reacting molecule or can prevent active metal migration (Guczi *et al.*, 1999; Goncalves *et al.*, 2006). Furthermore, the addition of a second metal could modify metal dispersion. A mixed oxide phase could be formed preventing surface mobility

of both metals and increasing dispersion of active metal. High metal dispersion could diminish deactivation of supported metal catalysts (De Correa *et al.*, 2005).

Recently, some publications have appeared which reported the enhancement of de-NO_x activity by adding noble metals into the transition metal catalysts or adding transition metal co-cations into catalyst such as Pd/Co/MOR (Bustamante *et al.*, 2002), In/Co/FER (Kubacka *et al.*, 2006) and Pd/Cu/MOR (Andrea *et al.*, 2007). The bimetallic catalysts was also more tolerant to water and showed better reversibility in activity after removal of water as reported by Quincoces *et al.* (2005) which used Pd/Co/SZ as the catalyst. The addition of 3.3 wt. % Co to Pd/ZSM-5 led to a stable NO conversion lasting more than 40 h in the presence of steam (Ogura *et al.*, 2000).

However, as described earlier, noble metals are expensive to use in this waste abatement. Thus, the transition metal co-cations are preferred in de-NO_x process. The function of co-cation in the catalysts is quite complex. At least, the oxidative activity and adsorption ability to gas reactants as well as the acidity of the supports can be influenced by the addition of co-cations. It was also experimentally found that the addition of a co-cation such as Ca or Ni to Cu ion-exchanged ZSM-5 zeolite (Cu/ZSM-5) could prevent the catalyst from deactivation caused by O₂ by forming oxides or some other compound or H₂O in the reaction gas (Yokomichi *et al.*, 2000).

2.3 ZSM-5 as a zeolite catalyst support

Catalyst support provides a means for spreading out active species to promote catalytic reaction. Desirable feature of catalyst support includes large surface area, high thermal stability under reaction conditions, high resistance to metal sintering,

high porosity to ease molecular diffusion and inertness to undesired reactions (Fogler, 1999). There are many types of catalyst supports ranging from metal oxides, perovskites, alumina, silica, and zeolite. However, zeolite-based catalysts have demonstrated interesting properties in SCR because they are relatively cheaper than metal oxide. Furthermore, the morphological and particular properties (well-defined crystalline structure, high internal surfaces area, uniform pores, good thermal stability) leads to shape-selective catalysis for reactions occurring within the micropore systems (Sobalik *et al.*, 2002).

Zeolites are porous crystalline aluminosilicates with the general formula $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2$ where n is the valence of the cation M and y may vary from 2 to infinite (Guisnet and Gilson, 2000). Structurally, zeolites comprise the assemblies of SiO_4 and AlO_4 tetrahedra joined together through the sharing of oxygen atoms with an open structure that can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^+ and others as shown in Figure 2.3. These cations can readily be exchanged for others in a contact solution.

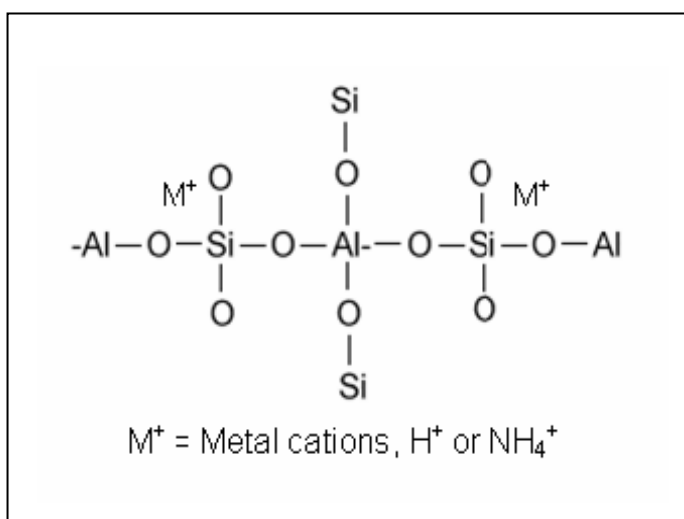


Figure 2.3: SiO_4 and AlO_4 units linked through shared oxygen (Guth and Kessler, 1999).

The tetrahedral formula of zeolites consists of SiO_2 and AlO_2^- with one negative charge resides at each tetrahedron in the framework containing aluminium in its centre. Silicon and aluminium in aluminosilicate zeolites are referred to as the T-atoms (Weitkamp, 2000). The T-atoms are located at the vertices and lines connecting them stand for T-O-T bonds.

International Union of Pure and Applied Chemistry (IUPAC) have classified the molecular sieve materials based on their pore size into three categories (Weitkamp, 2000):

Microporous material pore diameter < 2.0 nm

Mesoporous material $2.0 \text{ nm} \leq \text{pore diameter} \leq 50.0$ nm

Macroporous material pore diameter > 50.0 nm

In general, zeolite pore sizes fall into the microporous size and with ring size between 8 – 20 (Guth and Kessler, 1999). Zeolites have the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where the term "8 rings" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure.

Therefore, the pore openings for all rings of one size are not identical (Weitkamp, 2000).

Zeolite Socony Mobil 5, ZSM-5 has two types of pores, both formed by 10-membered oxygen rings. The first of these pores is straight and elliptical in cross section and are circular in cross section (Weitkamp, 2000) as shown in Figure 2.4.

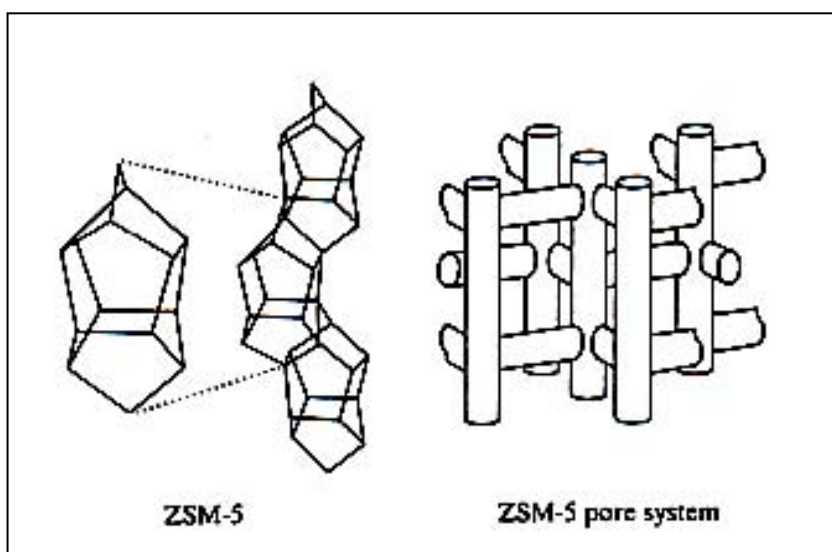


Figure 2.4: Framework structure of ZSM-5 (Weitkamp, 2000).

In the SCR process, the diffusion of reducing agent (i.e hydrocarbon) and the reactant (NO) play an isection; the second pores intersect the straight pores at right angles, in a zigzag patmportant role in obtaining higher conversion. Witzel *et al.* (1994) reported that two-dimensional structure of ZSM-5 zeolite enable reactant molecules to detour via adjacent channels whenever one of the channels was completely filled up by reactant gases. This make ZSM-5 recently gained attention in environment catalysis especially in reduction of NO_x emission (Guzman-Vargas *et al.*, 2005; Komvokis *et al.*, 2007; Shichi *et al.*, 2007).

2.3.1 ZSM-5 based catalyst

A number of ZSM-5-based catalysts have been developed in which the active phases are different metal such as manganese (Campa *et al.*, 1998), copper (Deeng *et al.*, 2004), cobalt and nickel (De Lucas *et al.*, 2005) and iron (Krocher *et al.*, 2006). The catalyst systems and the observed results are summarized in Table 2.2.

Table 2.2: Performance of ZSM-5-based catalysts tested for NO_x Reduction.

References	Catalyst	Conditions	Remarks
Campa <i>et al.</i> (1998)	Mn/ZSM-5	350°C - 500°C 1000 ppm NO 1000 ppm CH ₄	SCR decreased with increasing temperature (from 90% at 350°C to 50% at 500°C)
Deeng <i>et al.</i> (2004)	Cu/ZSM-5	375°C 1730 ppm NO 1280 ppm i-C ₄ H ₁₀	94 % reduction of NO and 4.6 % SCR-HC selectivity No structural changes in the catalyst after 48 h of continuous operation
De Lucas <i>et al.</i> (2005)	(Co and Ni)/ZSM-5	200°C - 500°C 1000 ppm NO 1000 ppm C ₃ H ₆	69.6 % conversion of NO at 400°C for Co/ZSM-5 and 76.6 % conversion of NO at 425°C for Ni/ZSM-5
Krocher <i>et al.</i> (2006)	Fe/ZSM-5	200°C - 600°C 1000 ppm NO 100-2000 ppm NH ₃	DeNO _x steadily increased from 200°C - 600°C, reaching > 90% for T > 450°C. It decreased at temperature beyond 600°C. However, 80 % conversion still achieved at 700°C.

From this summary, all the ZSM-5-based catalyst could obtain high reduction of NO_x which usually higher than 50 % in wider temperature range between 200 °C to 700 °C. Thus, zeolite ZSM-5 is the suitable support for SCR of NO_x purpose, based on the catalysts performance.