การศึกษาการเปรียบเทียบการเกิด N_2O ในระหว่างการรีดิวซ์แบบเลือกเกิดของ NO ด้วย NH_3 ในสภาวะที่มีและไม่มี O_2

นางสาวอัจฉรียาภรณ์ เรืองถาวรกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

COMPARATIVE STUDY OF N_2O FORMATION DURING THE SELECTIVE CATALYTIC REDUCTION OF NO BY NH_3 IN THE PRESENCE AND ABSENCE OF O_2 CONDITIONS

Miss Archareeyaporn Ruengthawornkul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2014

Thesis Title	COMPARATIVE STUDY OF N_2O FORMATION DURING THE SELECTIVE CATALYTIC REDUCTION OF NO BY NH_3 IN THE PRESENCE AND ABSENCE OF O_2 CONDITIONS
By	Miss Archareeyaporn Ruengthawornkul
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tharathon Mongkhonsi, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

....Chairman

(Professor Paisan Kittisupakorn, Ph.D.)

....Thesis Advisor

(Associate Professor Tharathon Mongkhonsi, Ph.D.)

....Examiner

(Paravee Vas-Umnuay, Ph.D.)

....External Examiner

(Thongchai Glinrun, D.Eng.)

อัจฉรียาภรณ์ เรืองถาวรกุล : การศึกษาการเปรียบเทียบการเกิด N_2O ในระหว่างการรีดิวซ์แบบเลือกเกิดของ NO ด้วย NH_3ในสภาวะที่มีและไม่มี O_2 (COMPARATIVE STUDY OF N_2O FORMATION DURING THE SELECTIVE CATALYTIC REDUCTION OF NO BY NH_3 IN THE PRESENCE AND ABSENCE OF O_2 CONDITIONS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ธราธร มงคลศรี, 79 หน้า.

งานวิจัยชิ้นนี้ทำการตรวจสอบการเกิด N_2O บนตัวเร่งปฏิกิริยา V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 และ V_2O_5-MoO_3/TiO_2 ระหว่างการเกิดปฏิกิริยาแบบเลือกเกิด (SCR) ด้วย NO และ NH_3 ตัวเร่งปฏิกิริยาทั้งหมดได้ผ่านการวิเคราะห์ด้วยกระบวนการดังต่อไปนี้ การวัดพื้นที่ผิว single point BET, XRD, FT-IR, NH_3-TPD, Pyridine adsorption, และ ICP-OES แก๊สขาเข้าระบบ SCR ประกอบด้วย NO 120 ppm, NH_3 120 ppm, SO_2 30 ppm, O_2 15% โดยปริมาตรและไอน้ำ 15% โดยปริมาตร โดยใช้ N_2 เป็นตัวเติมเต็มกระทั่งอัตราการไหลรวมเป็น 200 ml/min อุณหภูมิที่ใช้ในการทดลองคือ 120-450°C ทั้งนี้ในการทดลองปริมาณ NO ที่หายไปและปริมาณ N_2O ที่เกิดขึ้นทั้งหมดถูกตรวจวัดด้วย Gas Chromatography ยี่ห้อ Shimadzu รุ่น GC-2014 ด้วยตัวตรวจจับแบบอิเล็คตรอน (ECD) การทดลองนี้ได้ทำการตรวจสอบผลของ SO_2 ที่มีต่อการเกิด N_2O งานวิจัยนี้ยังได้ทำการทดลองผลของ O_2 ที่มีต่อการเกิด N_2O ระหว่างการเกิดปฏิกิริยา SCR บนตัวเร่งปฏิกิริยาทั้งหมดโดยการตัด O_2 ออกจากระบบ พบว่าปฏิกิริยา SCR ไม่สามารถดำเนินไปได้บนตัวเร่งปฏิกิริยา WO_3/TiO_2 และ V_2O_5-WO_3/TiO_2 ในขณะที่ปฏิกิริยา SCR สามารถเกิดขึ้นได้บ้างบนตัวเร่งปฏิกริยา V_2O_5/TiO_2, MoO_3/TiO_2 และ V_2O_5-MoO_3/TiO_2 อีกทั้งทำให้เกิด N_2O ปริมาณมากที่อุณหภูมิสูง ผลการทดลองทำให้ทราบว่า O^{-2} บนพื้นผิวตัวเร่งปฏิกิริยา V_2O_5/TiO_2, MoO_3/TiO_2 และ V_2O_5-MoO_3/TiO_2 มีส่วนร่วมในระหว่างการเกิดปฏิกิริยา SCR นอกจากนี้ผลการทดลองยังแสดงให้เห็นว่า O^{-2} บนตัวเร่งปฏิกิริยา MoO_3/TiO_2 และ V_2O_5-MoO_3/TiO_2 มีส่วนร่วมในการเพิ่มปริมาณ N_2O ที่เกิดขึ้นจากปฏิกิริยา SCR ผลการทดลองดังกล่าวทำให้ทราบว่า N_2O ที่เกิดขึ้นในระหว่างปฏิกิริยา SCR มาจากปฏิกิริยาระหว่าง NH_3 กับ O_2 มากกว่าปฏิกิริยาระหว่าง NH_3 และ NO

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
ปีการศึกษา	2557		

5670465621 : MAJOR CHEMICAL ENGINEERING
KEYWORDS: V2O5/TIO2 / MOO3/TIO2 / WO3/TIO2 / N2O / SCR / OXYGEN

ARCHAREEYAPORN RUENGTHAWORNKUL: COMPARATIVE STUDY OF N_2O FORMATION DURING THE SELECTIVE CATALYTIC REDUCTION OF NO BY NH_3 IN THE PRESENCE AND ABSENCE OF O_2 CONDITIONS. ADVISOR: ASSOC. PROF. THARATHON MONGKHONSI, Ph.D., 79 pp.

The present work investigates the formation of N_2O during the SCR of NO with NH_3 over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts. All catalysts are characterized by using BET surface area measurement, XRD, FT-IR, NH_3-TPD, Pyridine adsorption, and ICP-OES. The effluent gas in the SCR experimental contains 120 ppm NO, 120 ppm NH_3, 30 ppm SO_2, 15 vol% O_2, and 15 vol% H_2O, balanced with N_2. The reaction is carried out in the reaction temperature 120-450°C. A gas chromatograph Shimadzu GC-2014 equipped with an ECD is used to measure the amount of NO and N_2O in the effluent gas. The effect of SO_2 on the formation of N_2O during the SCR process over the catalysts is tested by removing SO_2 from the feed gas. The effect of O_2 on the formation of N_2O during the SCR process over the catalysts is tested by removing O_2 from the feed gas. The results show that O_2 is necessary for the SCR of NO by NH_3 over WO_3/TiO_2 and V_2O_5-WO_3/TiO_2 catalysts. The SCR of NO over V_2O_5/TiO_2, MoO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts can proceed in the absence of O_2, but at a higher reaction temperature with a large amount of N_2O form. The results demonstrate that lattice oxygen (O^{-2}) of V_2O_5/TiO_2, MoO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts can participate the SCR process at the high reaction temperature. O^{-2} on MoO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts is participate to increase N_2O formed from the SCR process. N_2O is formed from the reaction between NH_3 and O_2 rather than NO.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2014		

ACKNOWLEDGEMENTS

After long way with Master's degree in Chemical Engineer education, I realized that this thesis could not be a success without my Master's degree advisor, Assoc. Prof. Dr. Tharathon Mongkhonsi. I would like to express my gratitude to him for his guide for Master degree education, knowledge and invaluable help. I am grateful for his teaching in class and laboratory method for two year experience at Chulalongkorn University. I would like to thank him for his advice about life and this research in the right way. Lastly, I also would like to thank him for a chance in Master's degree at Chulalongkorn University and his trust in me.

I could not have today and succeed my thesis if I did not have advice from my Bachelor's degree advisor. For my parents, I gratefully thanked for their supports with financial and heart when I have a hard and lonely time in the big city.

I would like to thank people in Center of Excellence on Catalysis and Catalytic Reaction Engineer Laboratory, Chemical Engineering Department, Chulalongkorn University for their help and made a wonderful year in the year I work in lab.

CONTENTS

Page

TABLE CONTENTS

Page

FIGURE CONTENTS

Page

Page

CHAPTER I

INTRODUCTION

1.1 Background of this research

“Nitrogen oxides (NO_x)” is technical term which can refer to NO, N_2O, NO_2 or a combination of these gases. Nitrogen oxides are mainly produced during the combustion of fossil fuels and from some industrial processes. Among the oxides of nitrogen, NO or nitric oxide is the majority species released to the atmosphere. NO can form from the reaction between O_2 and N_2 gases at high temperature, for example during the combustion of fossil fuel according to the following reactions.

$$N_2 + O_2 \longrightarrow 2NO \qquad (1.1)$$

$$NO + 1/2O_2 \longrightarrow NO_2 \qquad (1.2)$$

Release of NO to environment causes several environmental problems such as acid rain and greenhouse gases. Therefore, elimination of NO from any exhaust gases containing NO is necessary. The Selective Catalytic Reduction (SCR) of NO by NH_3 is a technology that was developed to remove NO from exhaust gases, especially exhaust gas from power plants. In the SCR process, NH_3 is injected into the exhaust gas stream. NH_3 and NO will react with each other over a suitable catalyst and convert into N_2 and H_2O by two main reactions.

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \qquad (1.3)$$

$$4NH_3 + 2NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O \qquad (1.4)$$

The choice of catalyst use in the SCR process depends on operating temperature and the presence of SO_2 in the exhaust gas. MoO_3 works well with low temperature exhaust gas (i.e. less than 250°C) while V_2O_5 and WO_3 are more suitable for exhaust gases having intermediate temperature (i.e. between 200-400°C) and high temperature (i.e. higher than 400°C), respectively. If SO_2 exists in the exhaust gas stream, TiO_2 (anatase phase) is typically applied as catalyst support due to its resistance to sulfate formation.

The performance of the SCR catalyst is usually evaluated by determining the difference between the concentrations of NO in the feed and in the effluent gas from the reactor. The reaction requires a minimum reaction temperature to initiate the reaction and prevent the deposition of some solid compounds which may form from some side reactions downstream of the reactor. Too high reaction temperature, however, causes NH_3 reacts with O_2 and produce NO. Therefore, each catalyst has its own optimum operating temperature range, typically called windows.

The absence of NO from the effluent gas, however, does not always mean that NO is converted to a harmful reaction product (i.e. N_2). N_2O is a reaction product found during the SCR process but its formation is rarely reported due to the difficult in measuring the concentration of N_2O in the effluent gas. The formation of N_2O can attenuate the benefit of the SCR.

A common drawback shares by previous published research papers in the field of SCR is the neglect of N_2O formation. Only a few papers concern the formation of N_2O [1-51]. These papers, however, carried out their experiments in simulated exhaust gaseous streams having compositions different from the real exhaust gas. For example, the experiments were carried out in the absence of both H_2O and SO_2 [1-20], or in the presence of H_2O but absence of SO_2 [3,21,22]. Some published papers do concern the formation of N_2O in the simulated exhaust gas contains both H_2O and SO_2 [23]. Those published works, however, seem to concentrate on the exhaust composition similar to those generate from burning fuels having low H:C ratios such as coal or fuel oil. Such exhaust gases contain O_2 and H_2O at low concentrations.

The objective of the present work is to study the formation of N_2O during the SCR process over three catalysts i.e. V_2O_5/TiO_2, MoO_3/TiO_2, WO_3/TiO_2, V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3/TiO_2 in the presence and absence of O_2. The composition of the simulated exhaust gas used in our experiment is obtained from a power plant burning natural gas using gas turbine engine. Such exhaust gas contains high concentration of O_2 (15 vol%) and H_2O (15 vol%). In addition, the exhaust gas stream also contains SO_2 generated from burning sulfur compound impurity in the natural gas.

1.2 Scopes of the presented work.

The reaction conditions used in this research are as follows :

Reaction temperature : 120 – 450 °C

Feed gases : Total feed gas flow rate (dry basis) is 200 ml/min. The feed gas contains 120 ppm of NO, 120 ppm of NH_3, 15 vol% of vapor water, 30 ppm of SO_2 and use N_2 for balance.

The scope of this research is

1. Preparation of V_2O_5/TiO_2, MoO_3/TiO_2, WO_3/TiO_2, V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3/TiO_2 of catalysts using P25 as support by incipient wetness impregnation method.
2. Characterization the prepared catalysts using the following methods :
    - 2.1 X-ray diffraction technique (XRD) to determine crystal structure.
    - 2.2 Nitrogen physisorption to determine surface area.
    - 2.3 Inductively Couple Plasma-Optical Emission Spectroscopy (ICP-OES) to determine amount of metal composition of the catalysts.
    - 2.4 Temperature programmed desorption of NH_3 (NH_3-TPD) to determine the amount of acid site on catalyst surface.
    - 2.5 Pyridine adsorption to determine the total amount of acid sites on the catalyst surface.
    - 2.6 Fourier transforms infrared (FT-IR) to determine functional group on the catalyst surface.
3. Catalytic activity for NO reduction testing.
4. Measure N_2O in the effluent gas from the SCR of NO by NH_3.
5. Study the effect of SO_2 on the formation of N_2O during the SCR process.

1.3 Arrangement of this Thesis.

This thesis is arranged in the following manner :

- Chapter I (this chapter) gives background of this research.
- Previous research works related to the presented work are summarized in Chapter II.
- Chapter III gives details of characterization and experimental methods.
- Experimental results and discussion are gathered in Chapter IV.
- Overall conclusions emerged from this research is reported in Chapter V.
- Finally, sample of calculation and raw data are included in the Appendices.

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter gives a brief introduction to the SCR process in section 2.1. Section 2.2 and 2.3 summarize research papers relate to the SCR processes using oxides of V, W, and Mo as catalysts.

2.1 Selective Catalytic Reduction (SCR) of NO by NH_3

NO_x emissions cause environment problems such as photochemical smog, ozone depletion and acid rain for a long time. In 1970s, the Selective Catalytic Reduction technology has been first developed in Japan. This technology is developed to reduced NO_x. At present the SCR technology has been worldwide used in industry processes for the reduction of NO emission. In this processes, ammonia is injected into emission gases. The reaction will occur on surface of a catalyst, according to the following reaction [27-30] :

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \qquad (2.1)$$

$$4NH_3 + 4NO + 3O_2 \longrightarrow 4N_2O + 6H_2O \qquad (2.2)$$

Concurrently, while ammonia reacts with NO in the emission gases, ammonia will also reacts with NO_2 according to the following reaction :

$$4NH_3 + 2\,NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O \qquad (2.3)$$

At temperature above 350 °C in the SCR feed stream, ammonia can reacts directly with oxygen. This reaction is a side reaction and it is call ammonia oxidation reaction. Ammonia oxidation produces N_2 (desired product) and N_2O and NO (undesired products) follows :

$$2NH_3 + 3/2O_2 \longrightarrow N_2 + 3H_2O \qquad (2.6)$$

$$2NH_3 + 2O_2 \longrightarrow N_2O + 3H_2O \qquad (2.7)$$

$$2NH_3 + 5/2O_2 \longrightarrow 2NO + 3H_2O \qquad (2.8)$$

2.2 Catalysts for the Selective Catalytic Reduction of NO by NH_3

V_2O_5 , WO_3 and MoO_3 oxides are widely used as catalysts on the SCR of NO by NH_3. V_2O_5 catalyst is the most active in the intermediate temperature range but V_2O_5 can produce an undesired byproduct. SO_3 can form from the oxidation of SO_2 over V_2O_5[27]. The formation of SO_3 leads to catalyst deactivation due to the deposition of $(NH_4)_2SO_4$ and NH_4HSO_4 on the catalyst surface according to the following reaction

$$2SO_2 + O_2 \longrightarrow 2SO_3 \qquad (2.9)$$

$$SO_3 + NH_3 + H_2O \longrightarrow NH_4HSO_4 \qquad (2.10)$$

$$SO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2SO_4 \qquad (2.11)$$

In low reaction temperature region, MoO_3 can work better than V_2O_5. However, MoO_3 is prone to oxidize NH_3 to NO at high temperature. WO_3 is not quite active for the oxidation of NH_3 but active for the SCR at high temperature. In the presence of SO_2, TiO_2 is suitable support because its resistance to sulfate formation

2.3 Comment on previous works

Review of literatures illustration in Table 2.1 shows that, to be best of our knowledge, there is no research group carried out study with simulated exhaust gas having high concentration of oxygen and water vapor. In addition, the formation of N_2O is neglected in most research works. Because of this reason, there is necessity to investigate the formation of N_2O in an exhaust gas having high concentration of both oxygen and water vapor. This is the main objection of this research.

Table 2.1 Literature review about the feed composition on feed gas of selective catalytic reduction (SCR) of NO by NH_3

Catalyst	Feed								Temperature °C	Measure	Reference/Comments
	NO ppm	NH_3 ppm	O_2 vol%	H_2O vol%	SO_2 ppm	other	Balance	Total ml/min			
MoO_3/TiO_2	0.1vol%	0.1vol%	3	-	-	-	He	50	250	NO	[22]
V_2O_5-WO_3/TiO_2	400	400	4	8	800	-	-	3300 Standart	350	NO	[23]
V_2O_5-MoO_3/TiO_2	400	400	4	8	800	-	-	3300 Standart	350	NO	[23]
V_2O_5/TiO_2	800	800	9000ppm	-	-	-	He	120	152-477	NO/N_2O	[24]
MoO_3/TiO_2	800	800	9000ppm	-	-	-	He	120	152-477	NO/N_2O	[24]
V_2O_5-MoO_3/TiO_2	800	800	9000ppm	-	-	-	He	120	152-477	NO/N_2O	[24]
V_2O_5/TiO_2	600	700	2	-	-	Ar	He	900	260-400	NO	[25]
WO_3/TiO_2	600	700	2	-	-	Ar	He	900	260-400	NO	[25]
V_2O_5/TiO_2	74 Pa	78 Pa	6000 Pa	-	-	-	-	900	240-280	NO	[26]
WO_3/TiO_2	74 Pa	78 Pa	6000 Pa	-	-	-	-	900	240-280	NO	[26]

Table 2.1 Literature review about the feed composition on feed gas of selective catalytic reduction (SCR) of NO by NH_3

Catalyst	Feed								Temperature °C	Measure	Reference/Comments
	NO ppm	NH_3 ppm	O_2 vol%	H_2O vol%	SO_2 ppm	other	Balance	Total ml/min			
V_2O_5/TiO_2	1000	1000	2	8	1000	-	He	500	200-450	$NO/NO_2/N_2O$	[27]
V_2O_5-WO_3/TiO_2	0-750	0-840	2	-	-	-	-	$1.4x10^{5}$ h^{-1}	280-400	NO	[28]
MoO_3/TiO_2	800	800	4	-	-	-	N_2	150	100-450	NO	[29]
$3V_2O_5$-$7WO_3/TiO_2$	1000	1000	3.5	2.7	-	H_2	N_2	300	250	NO	[30]
V_2O_5/TiO_2	800	800	3	6	500	-	N_2	500	150-400	NO/SO_2	[31]
WO_3-V_2O_5/TiO_2 (Sti-PILC)	0.1 v%	0.1 v%	2.5	-	-	-	He	100	100-400	NO	[32] Sti-PILC is Sulfated Ti-pillared clay
V_2O_5/TiO_2	910	1000	4	-	-	-	N_2	500	310	NO	[33]
V_2O_5-WO_3/TiO_2	1000	1000	8	5	-	CO,CO_2	N_2	100	250-450	NOx	[34]
V_2O_5/TiO_2	500	500	5	-	-	-	N_2	1000	150-550	$NO/NO_2/N_2O$	[35]

Table 2.1 Literature review about the feed composition on feed gas of selective catalytic reduction (SCR) of NO by NH_3

Catalyst	Feed								Temperature °C	Measure	Reference/Comments
	NO ppm	NH_3 ppm	O_2 vol%	H_2O vol%	SO_2 ppm	other	Balance	Total ml/min			
WO_3/TiO_2	500	500	5	-	-	-	N_2	1000	150-550	$NO/NO_2/N_2O$	[35]
V_2O_5/TiO_2	500	500	6	2.5	200	-	N_2	500	100-300	NO/NO_2	[36]
WO_3/TiO_2	500	500	5	-	-	-	N_2	200	350-600	NO/NO_2	[37]
V_2O_5-WO_3/TiO_2	500	500	3	-	-	-	N_2	300	150-500	NOx/N_2O	[38]
V_2O_5-WO_3/TiO_2	1000	1000	2	-	-	-	He	183.3	150-450	NO	[39]
V_2O_5-WO_3/TiO_2	500	500	10	10		-	N_2	$18\text{-}75\times10^3 h^{-1}$	180-250	NO	[40]
WO_3-SiO_2/TiO_2	200	200	2×10^4 ppm	10	-	-	N_2	300	200-450	NO	[41]
WO_3/TiO_2	500	500	3	5.5	-	-	N_2	200	100-500	$NO/NO_2/N_2O$	[42]
V_2O_5-WO_3/TiO_2	500	500	3	5.5	-	-	N_2	200	100-500	$NO/NO_2/N_2O$	[42]
V_2O_5/TiO_2	200	200	0-5	-	-	-	N_2	500	100-400	NO/NO_2	[43]

Table 2.1 Literature review about the feed composition on feed gas of selective catalytic reduction (SCR) of NO by NH_3

Catalyst	Feed								Temperature °C	Measure	Reference/Comments
	NO ppm	NH_3 ppm	O_2 vol%	H_2O vol%	SO_2 ppm	other	Balance	Total ml/min			
V_2O_5 /TiO_2	1000	1100	5	-	-	-	N_2	1000	200-550	NO	[44]
WO_3 /TiO_2	1000	1100	5	-	-	-	N_2	1000	200-550	NO	[44]
V_2O_5/TiO_2	500	500	5	-	-	-	N_2	150	240-390	NOx	[45]
V_2O_5/ TiO_2	500	500	5	-	-	-	N_2	1000	150-550	NO/NO_2/N_2O	[46]
WO_3/TiO_2	500	500	5	-	-	-	N_2	1000	150-550	NO/NO_2/N_2O	[46]
V_2O_5-WO_3/TiO_2	1000	1000	10	5	100	-	N_2	2500	50-600	NO/N_2O/NO_2/S_2O	[47]
MoO_3-CeO_2/TiO_2	500	500	5	5	50	-	He	300	200-400	NO/NO_2	[48]
V_2O_5-WO_3/TiO_2	600	480	3	10	2000	-	N_2	$1.4x10^3 h^{-1}$	150-450	NO	[49]
V_2O_5/TiO_2	500	500	2	-	-	-	N_2	$4x10^4 h^{-1}$	150-400	NOx /N_2O	[50]
V_2O_5-WO_3/TiO_2	500	600	5	-	-	-	N_2	150	150	NO/NO_2	[51]

CHAPTER III

EXPERIMENTS

This chapter gives detail of catalyst preparation method in section 3.1. Section 3.2 consists of characterization techniques such as X-ray diffraction, Nitrogen physisorption, NH_3-TPD, FT-IR and ICP-OES method. Finally, section 3.3 explains catalytic activity evaluation procedures.

3.1 Catalyst preparation

3.1.1 Chemicals

In the catalyst preparation process, chemicals listed in Table 3.1 below are used.

Table 3.1 Chemicals are used in catalyst preparation.

Chemicals	**Supplier**
Commercial grade titanium dioxide (P25)	Aeroxide
Ammonium metavanadate, 99.99%	Aldrich
Ammonium metatungstate hydrate, 99.99%	Aldrich
Ammonium molybdate tetrahydrate, 99.99%	Aldrich
Nitric acid 65%	Aldrich
Oxalic acid hydrate	Fluka

3.1.2 Catalysts preparation

Incipient wetness impregnation method was used to prepared V_2O_5/TiO_2, MoO_3/ TiO_2, WO_3/ TiO_2, V_2O_5-MoO_3/ TiO_2 and V_2O_5-WO_3/ TiO_2 catalysts. The detail of this method is as follows :

(1) Preparation of V_2O_5/ TiO_2, MoO_3/ TiO_2 and WO_3/TiO_2 catalysts.

For V_2O_5/TiO_2, ammonium metavanadate was used as precursor, and TiO_2 was used as support. The method begins with dissolving ammonium metavanadate and oxalic acid hydrate in water. Then the obtained solution was slowly added on TiO_2 support. Next, the impregnated support was dried at 110 °C for 12 hr. Finally the dried impregnated support was calcined in air at 500 °C for 2 hr to convert to V_2O_5/TiO_2 catalyst.

MoO_3 and WO_3 were prepared by the same method described in the above paragraph. Ammonium molybdate tetrahydrateand and ammonium metatungstate hydrate were used as precursors for MoO_3 and WO_3, respectively. TiO_2 was still used as support.

(2) Preparation of V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3/TiO_2 catalysts.

For V_2O_5-MoO_3/TiO_2, ammonium metavanadate was used as precursor and TiO_2 was used as support. The method begins with dissolving ammonium metavanadate and oxalic acid hydrate in water. Then the obtained ammonium metavanadate solution was slowly added on TiO_2 support. Next, the impregnated support was dried at 110 °C for 12 hr. Next, ammonium molybdate tetrahydrate and oxalic acid are dissolved in water. Then the obtained ammonium molybdate tetrahydrate and oxalic acid solution was slowly added on TiO_2 support. The impregnated support was dried again at 110 °C for 12 hr. Finally the dried impregnated support was calcined in air at 500 °C for 2 hr to convert to V_2O_5-MoO_3/TiO_2 catalyst.

For V_2O_5-WO_3/TiO_2, ammonium metavanadate was used as precursor and TiO_2 was used as support. The method begins with dissolved ammonium metavanadate and oxalic acid hydrate in water. Then the obtained ammonium metavanadate solution was slowly added on TiO_2 support. Next, the impregnated support was dried at 110 °C for 12 hr. Next, ammonium metatungstate hydrate and oxalic acid are dissolved in water. Then the obtained ammonium metatungstate hydrate and oxalic acid solution was slowly added on TiO_2 support. The impregnated support was dried again at 110 °C for 12 hr. Finally the dried impregnated support was calcined in air at 500 °C for 2 hr to convert to V_2O_5-WO_3/TiO_2 catalyst.

3.2 Characterization of catalysts

In this experiment, the prepared catalysts were characterized by using different characterization techniques as follows :

3.2.1 BET surface area measurement

To measurement the surface area of each catalyst, nitrogen adsorption at -196 °C, single point BET technique was used. The measurement was carried out on Micromeritrics Chemisorb 2750. Prior the analysis, 0.1 g of catalysts was degassed at 200 °C in He flow for 4 hr. Then He was switched to 15%N_2/He. The sample was allowed to adsorb N_2 at liquid N_2 boiling temperature, -196 °C. After adsorption, the adsorb N2 was removed from the sample surface by removing liquid N_2 bath from the sample. The surface area of catalyst can be calculated from the amount of desorb N_2.

3.2.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

The inductively-coupled plasma optical emission spectroscopy (ICP-OES), Perkin Elmer Optima 2100 DV, was used to identify the percentage of metal loading over TiO_2 catalyst. This method used 0.01 g sample of catalysts. The sample was dissolved in dissolving of 15 g $(NH_3)_2SO_4$ and 20 ml of H_2SO_4, stirred vigorously until the mixing solution became homogenous and made volume up to 100 ml by added water in mixing solution.

3.2.3 Acid site

(1) NH_3 Temperature programmed desorption (NH_3-TPD)

NH_3–TPD (Micromeritrics chemisorb 2750) was used for measurement strength and amount of acid site on catalysts surface. The amount of NH_3 adsorbed on the surface of catalysts was determined by thermal conductivity detector (TCD). 0.1 g of catalyst was placed inside a sample tube and preheated in 50 ml/min of He from ambient to 200 ^{O}C (heating rate 10 ^{O}C/min) and hold at that temperature for 2 hr to remove impurities. After cooling down to 120 ^{O}C, 0.5 ml of 10000 ppm NH_3 in He was injected to the sample. The injection was repeated until the sample became saturated with NH_3. Then the catalyst was heated up again to 500 ^{O}C (heating rate 10 ^{O}C/min) in order to remove the adsorb NH_3.

(2) Pyridine adsorption

Pyridine adsorption technique was used for measurement the overall acid site on the surface of the catalyst. 0.1 g of catalyst sample was packed in a stainless steel sample tube placed in a gas chromatograph (Shimadzu GC-8A) equipped with a flame ionization detector (FID). The oven temperature was controlled at 150 ^{O}C. The measurement was carried out by injecting 0.2 μl of pyridine to the sample. The amount of unadsorbed pyridine was recorded. The injection was repeated until the sample became saturated with pyridine. The total of acid site on surface of catalyst was calculated from the summation of pyridine adsorbed on the surface of catalyst.

3.2.4 X-Ray Diffraction (XRD)

Crystal structure of all catalysts was determined by X-Ray Diffraction (XRD) technique. The characterization was performed by using D8 Advance Bruker AXS. CuKα was used as a radiation source (wave length is 0.154056 nm). The spectra were collected in the region of 2Θ between 20 ° to 80 ° with step size 0.02 ° and 0.6 nm of slit width.

3.2.5 Fourier transforms infrared (FT-IR)

FT-IR, Nicolet model 6700 of IR Spectrometer, was used to identify the functional group on surface of each catalyst. The spectra were recorded in wave range of infrared (400-4000 cm^{-1}).

3.3 Catalytic activity testing

Catalytic activity test consists with the SCR NO by NH_3, The SCR of NO by NH_3 in absence of oxygen condition, formation of N_2O during the SCR of NO with NH_3 over TiO_2 and effect of SO_3 on The SCR processes in absence of O_2 and SO_2 for each catalyst.

The reactions were carried out in a 3/8 in. O.D. stainless steel fixed-bed reactor packed with 0.05 g of quartz wool and 0.1 g of catalyst. Testing temperatures are between 120-450 °C. The gas outlet compositions were determined by using a gas chromatograph Shimadzu GC-2014 equipped with an electron capture detector (ECD). Feed gas used in the SCR operation contains 120 ppm NO, 120 ppm NH_3, 15vol% O_2, 15 vol% H_2O, 30 ppm SO_2 and balance with N_2. Total flow rate 200 ml/min (dry basis).

NO and N_2O generated from the reaction between NH_3 and NO were also quantitatively analyzed by using feed composition in the SCR of NO by NH_3 that show in Table 3.2. In addition, the SCR performance evaluation of each catalyst in the absence of O_2 and SO_2 were also performed by removing O_2 and SO_2 out of the feed gas stream.

Table 3.2 Feed Composition .

Reaction	NO (ppm)	NH_3 (ppm)	O_2 (vol%)	H_2O (vol%)	SO_2 (ppm)	N_2	Flow rate (ml/min)
SCR 1 Stablility test	120	120	15	15	30	Balance	200
SCR 2 NO conversion	120	120	15	15	30	Balance	200
SCR 3 N_2O Formation	120	120	15	15	30	Balance	200
SCR absence of O_2 NO conversion	120	120	-	15	30	Balance	200
SCR absence of O_2 N_2O Formation	120	120	-	15	30	Balance	200
SCR absence of SO_2 NO conversion	120	120	15	15	-	Balance	200
SCR absence of SO_2 N_2O Formation	120	120	15	15	-	Balance	200

Table 3.3 SCR condition of Shimadzu GC-2014 in used.

Lists	Detection gases	
	NO	N_2O
Detector	ECD	ECD
Detector Temperature	200 °C	200 °C
Column	Hyasep-DB	Hyasep-DB
Column Temperature	40 °C	150 °C
Inlet Column Diameter	0.1	0.1
Outlet Column Diameter	2	2
Carrier gas	N_2	N_2

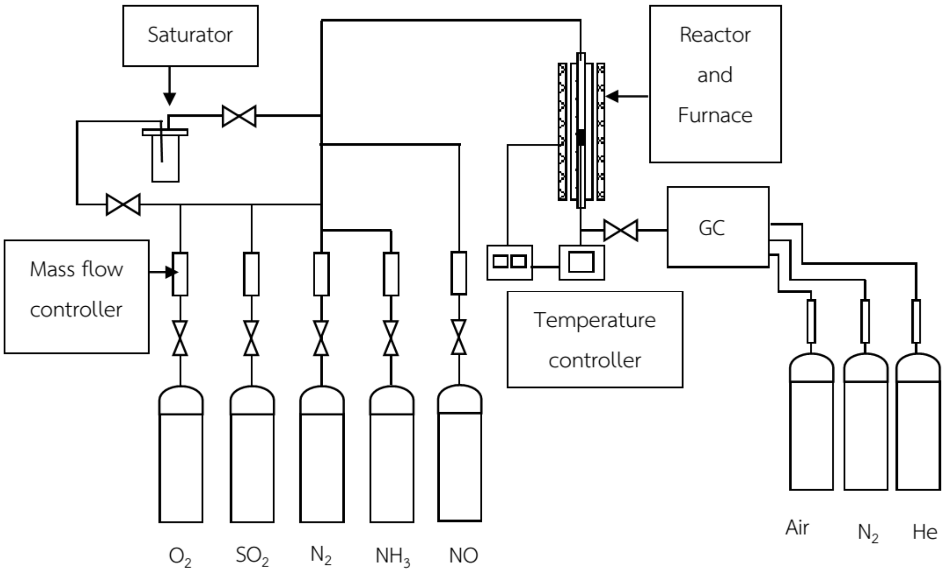

Figure 3.1 Flow diagram of Selective Catalytic Reduction of NO with NH_3 system.

CHAPTER IV

RESULTS AND DISCUSSIONS

This chapter shows and discusses results of characterization of catalyst and catalytic activity testing of V_2O_5, WO_3, MoO_3, V_2O_5-WO_3 and V_2O_5-MoO_3 catalysts supported on TiO_2 support. The chapter is arranged in the following manner, section 4.1 describes characterization results, section 4.2 is catalytic activity testing, section 4.3 the effect of SO_2 on the SCR of NO by NH_3 and section 4.4 the effect of O_2 on the SCR of NO by NH_3.

4.1 Characterization of catalysts

This section reports BET surface area measurement, elemental compositions, surface acidity, X-ray diffraction spectroscopy (XRD) and Fourier transform infrared (FT-IR) spectroscopy results.

4.1.1 BET Surfaces area measurement and elemental compositions

Surface area measurement was carried out using N_2 adsorption technique. The surface areas were calculated using BET theorem. Elemental composition was measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The results are summarized in Table 4.1 showed below :

Table 4.1 BET surface area and %metal composition for each catalyst.

Catalyst	BET Surface area (m^2/g)	Metal composition
TiO_2	24.6	-
V_2O_5/TiO_2	28.1	1.87 wt% V_2O_5
WO_3/TiO_2	30.3	22.95 wt% WO_3
MoO_3/TiO_2	33.0	3.96 wt% MoO_3
V_2O_5-WO_3/TiO_2	25.0	1.96 wt% V_2O_5 and 19.72 wt% WO_3
V_2O_5-MoO_3/TiO_2	28.6	2.14 wt% V_2O_5 and 3.50 wt% MoO_3

In Table 4.2, we can observe that surface areas of each catalyst are approximately around 30.0 m^2/g. In addition, it should be noted here that the surface areas of the prepared catalyst are slightly higher than the surface area of the pure support. A possible explanation is the decomposition of metal salts, which produce gaseous products, causes some changing on TiO_2 (P25) support which results in a slight increase in the surface area of the catalyst. Another possible explanation is the structure of the commercial TiO_2 (P25) is not stable. Explosion to high temperature during the calcination step completely converts all the structure into a more stable form, which has higher surface area. This explanation comes from the observation that the volume of TiO_2 (P25) powder decreases significantly after calcination.

4.1.2 Acid site

Surface acidity of each catalysts are measured by using NH_3 temperature programmed desorption (NH_3-TPD) and pyridine adsorption techniques. The measurement results are shown in Table 4.2.

According to the SCR mechanism, the reaction begins with the adsorption of NH_3 on the acidic site of the catalyst surface. The capability of the catalyst surface to retain NH_3 molecule depends on reaction temperature. Usually, the higher the reaction temperature, the lower the amount of NH_3 on the catalyst surface. The amount of adsorbed pyridine represents total acid site on the catalyst surface. The amount of NH_3 desorbed at different temperatures, as can be calculated from NH_3-TPD measurement represents amount of surface acid site which cannot used as active site at that reaction temperature.

From data show in Table 4.2, the amount of acid site which cannot retain NH_3 molecule at temperature higher than 500 °C (NH_3-TPD result) is much less than the total acid site (pyridine adsorption). From this reason, the changing in conversion and selectivity of the reaction at different reaction temperature should not be the result of the changing amount of NH_3 adsorption on the surface of catalyst.

Table 4.2 Acid site of each catalysts by NH_3 temperature programmed desorption (NH_3-TPD) and Pyridine adsorption technique.

Catalyst	Acid Site (μmol/g)	
	Pyridine adsorption	NH_3 – TPD
TiO_2	157.96	0.74
V_2O_5/TiO_2	74.92	0.34
WO_3/TiO_2	131.13	1.06
MoO_3/TiO_2	91.10	0.07
V_2O_5-WO_3/TiO_2	129.29	0.08
V_2O_5-MoO_3/TiO_2	103.58	0.08

4.1.3 X-Ray Diffraction (XRD)

The results of XRD analysis shown in Figure 4.1 are detected in the 2θ region 20-80 degree. After being calcined at 500 °C for 4 hr, TiO_2 anatase pattern of each catalyst does not change to TiO_2-rutile. It means that in this experiment, reaction temperature does not cause the deactivation of the catalyst due to phase transformation of TiO_2 support, because the maximum reaction temperature used in our experiments is only 450 °C.

The disappearance of diffraction pattern of other metal oxide compound (V, Mo, and W) indicates that the oxides of V, Mo, and W are well dispersed on the catalyst surface or exist in the amorphous form.

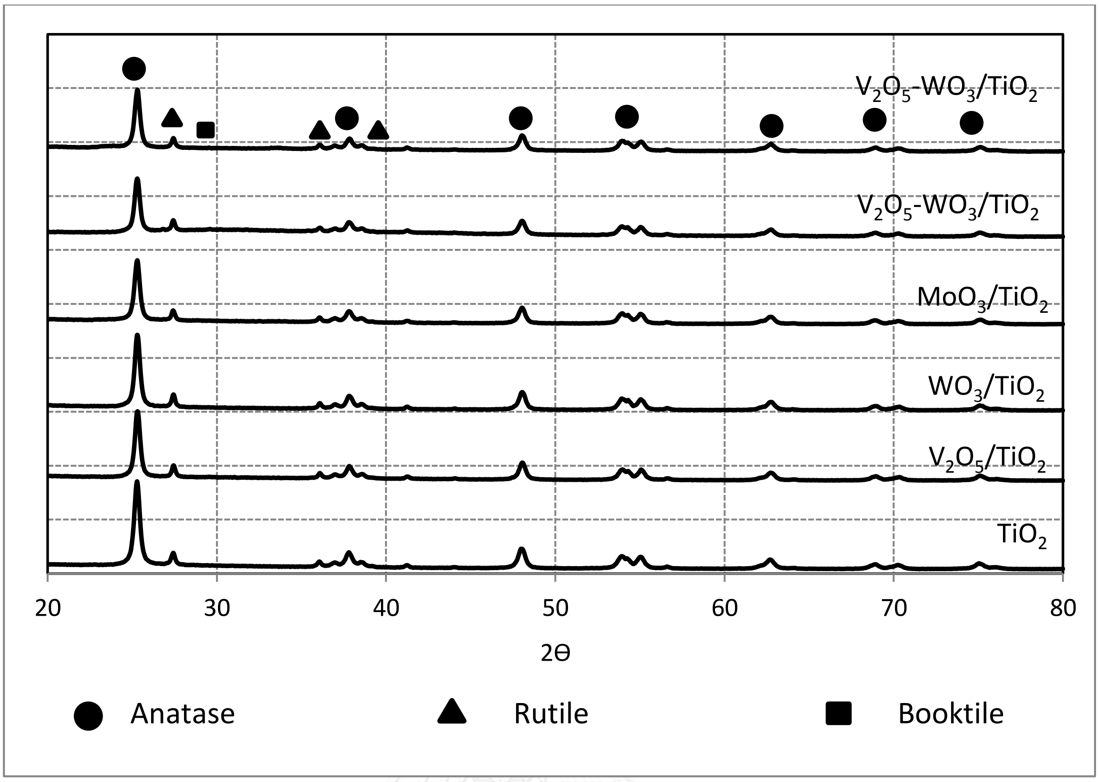

Figure 4.1 XRD pattern for each catalyst.

4.1.4 Fourier transforms infrared (FT-IR).

FT-IR spectroscopy is used for studying functional group on the catalyst surface. FT-IR spectrum of each catalyst is recorded in wave number range 500-1500 cm^{-1} by using Nicolet impact 6700 IR spectrometer. FT-IR spectra in Figure 4.2 shows that TiO_2 anatase strongly absorbed IR in the region 700-660 cm^{-1}. From the result shown in figure 4.2, the IR spectra of all catalyst samples show similar pattern, i.e. a broad peak between 550-1000cm^{-1}. Therefore, other metal oxide species apart from TiO_2 cannot be specified.

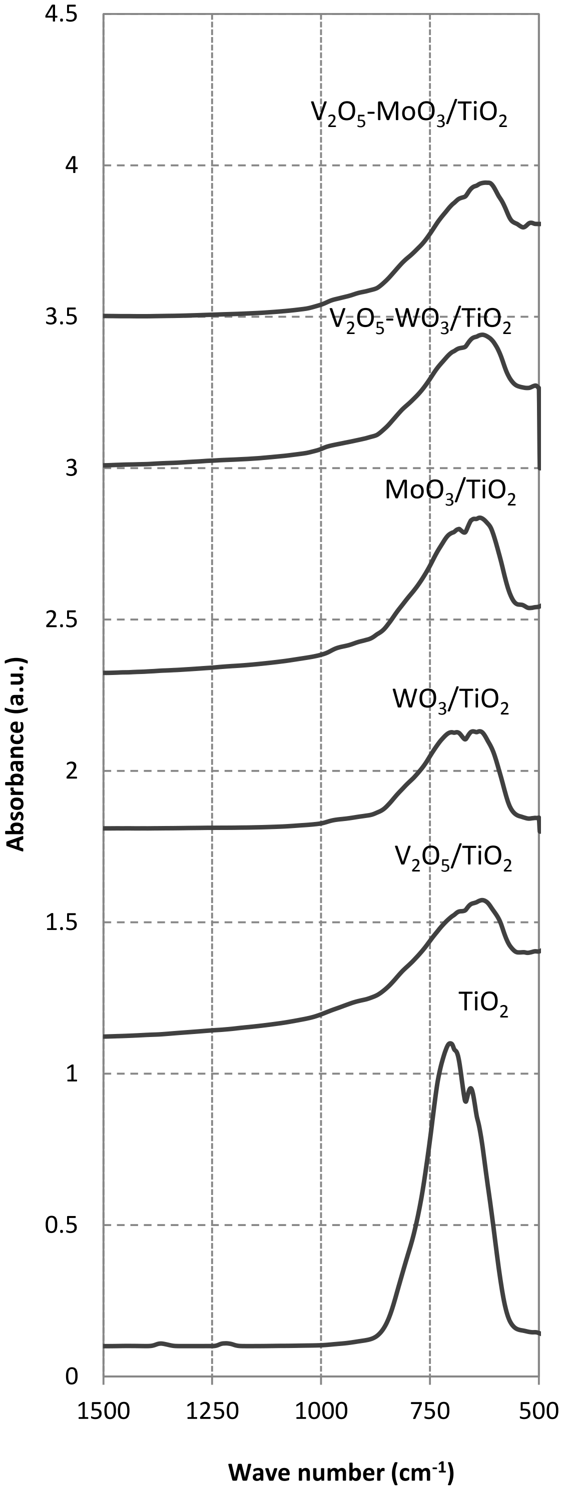

Figure 4.2 FT-IR spectra for TiO_2, V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts.

4.2 Catalytic activity testing

This section reports catalytic activity testing of each catalyst. The experimental results include the formation of N_2O in the SCR of NO by NH_3, stablility of each of catalyst, the effects of O_2 and SO_2 on the formation of N_2O in the SCR of NO by NH_3 on each catalyst.

In the following section NO conversion and NOx conversion are calculated from the following equations :

$$NOconversion \quad = \frac{NO\ in - NO\ out}{NO\ in} \times 100 \qquad 4.1$$

$$NOx\ conversion = \frac{NOin - (NOout + N2Oout)}{NOin} \times 100 \qquad 4.2$$

4.2.1 Stablility test

Each catalyst before catalytic testing must be confirmed that its structure has stability. To confirm the stability of the structure of each catalyst, the catalyst sample was heated to 120 °C and held at that temperature for 1 hr before measuring NO in the effluent gas. Then the catalyst sample was heated up to 450 °C and held at that temperature for 1 hr before measuring NO in the effluent gas again. After that the catalyst sample was cooled down to 120 °C and the heating process was repeated again. If the NO conversion measured at the same temperature from both run are approximately the same the catalyst was considered stable and can be used in the subsequent experiment. If the NO conversions are quite different, the heating process will be repeated again. Table 4.3 summarizes NO conversion obtained from the last two runs of each catalyst.

Table 4.3 Stability test for V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts.

Catalyst	%NO conversion			
	Temperature			
	120 °C		450 °C	
	Test 1	Test 2	Test 1	Test 2
V_2O_5/TiO_2	0.00	0.00	36.99	31.20
WO_3/TiO_2	0.00	0.00	34.50	26.90
MoO_3/TiO_2	0.00	0.00	16.83	16.29
V_2O_5-WO_3/TiO_2	0.00	0.00	62.25	67.08
V_2O_5-MoO_3/TiO_2	0.00	0.00	54.36	46.46

4.2.2 The Selective Catalytic Reduction of NO by NH_3

In this section, the results consist of NO conversion, N_2O formation and NOx conversion on the SCR of NO by NH_3 over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts. This experiment is operated using gas composition containing 120 ppm of NO, 120 ppm of NH_3, 30 ppm of SO_2, 15 vol% of O_2 and 15 vol% of H_2O. Total volumetric flow rate is 200 ml/min. The experiment was carried out in the reaction temperature range 120-450 °C. The catalysts uses in this experiment were the catalyst passes the testing in section 4.2.1

4.2.2.1 V_2O_5/TiO_2

The results of SCR on V_2O_5/TiO_2 catalyst are shown in Figures 4.3 and 4.4. For this catalyst, the reaction begins at a reaction temperature around 150 °C. NO conversion begins at 150 °C and increases until reaching a maximum, 54.10%, at 300 °C. Beyond this reaction temperature, NO conversion gradually decreases to around 20% at 450 °C.

N_2O is firstly observed at a reaction temperature around 400 °C, 5.2 ppm. The concentration of N_2O slowly increases to 9.7 ppm at 450 °C.

NOx conversion profile showed in Figure 4.4 is similar to NO conversion profile showed in Figure 4.3. The difference is in the reaction temperature region 400-450 °C where the values of NOx conversion are lower than the values of NO conversion in the same temperature region. This is due to the formation of N_2O in that reaction temperature region.

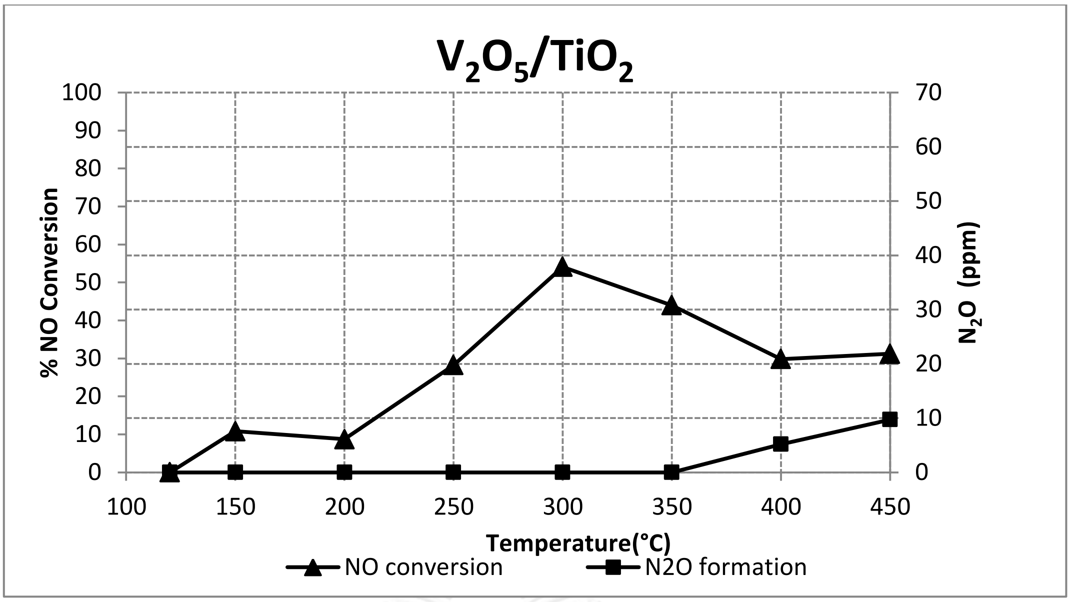

Figure 4.3 NO conversion and N_2O formation during the SCR reaction on V_2O_5/TiO_2 catalyst.

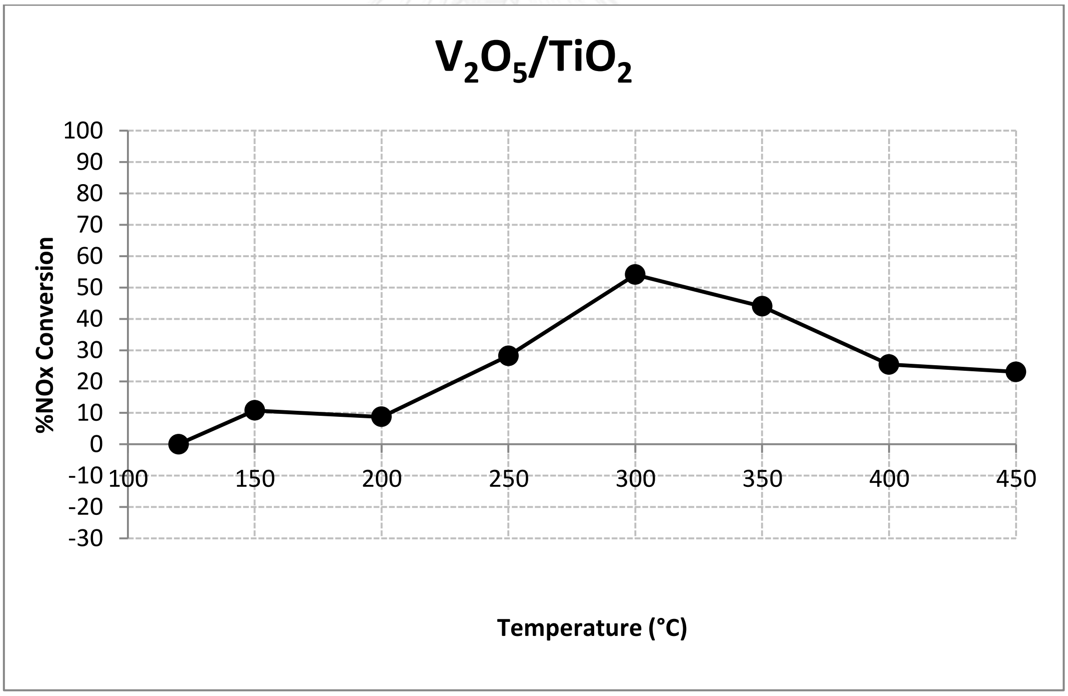

Figure 4.4 NOx conversion during the SCR reaction on V_2O_5/TiO_2 catalyst.

4.2.2.2 WO_3/TiO_2

The results of SCR on WO_3/TiO_2 catalyst are shown in Figures 4.5 and 4.6. For this catalyst, the reaction begins at a reaction temperature around 250 °C. NO conversion begins at 250 °C and increases until reaching a maximum, 37.4%, at 400 °C. Beyond this reaction temperature NO conversion gradually decreases to around 18% at 450 °C. N_2O cannot be observed during the reaction that makes NOx conversion profile showed in Figure 4.6 is the same profile with NO conversion profile showed in Figure 4.5.

4.2.2.3 MoO_3/TiO_2

The results of SCR on MoO_3/TiO_2 catalyst are shown in Figures 4.7 and 4.8. For this catalyst, the reaction begins at a reaction temperature around 250 °C. NO conversion begins at 250 °C and increases until reaching a maximum, about 41.23%, at 350 °C. Beyond this reaction temperature NO conversion slowly decreases to around 10% at 400 °C.

N_2O is firstly observed at the reaction temperature 250 °C, about 5.8 ppm. The concentration of N_2O increases to 43.3 ppm at 400 °C. It should be noted here that this catalyst produces a large amount of N_2O during the SCR process.

NOx conversion profile showed in Figure 4.8 is quite different from NO conversion profile showed in Figure 4.7. This is due to in the reaction temperature region 250-450 °C the formation of N_2O is very high. The high concentration of N_2O formed can offset the amount of NO converted. In term of NOx conversion, the maximum conversion achieved is only about 15% at 350 °C.

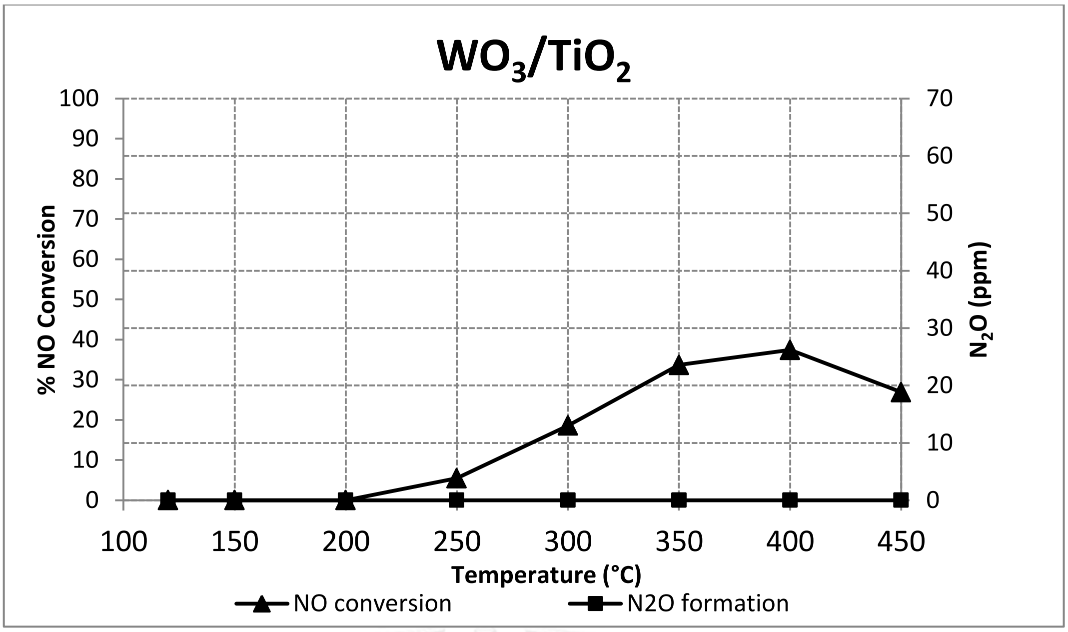

Figure 4.5 NO conversion and N_2O formation during the SCR reaction on WO_3/TiO_2 catalyst.

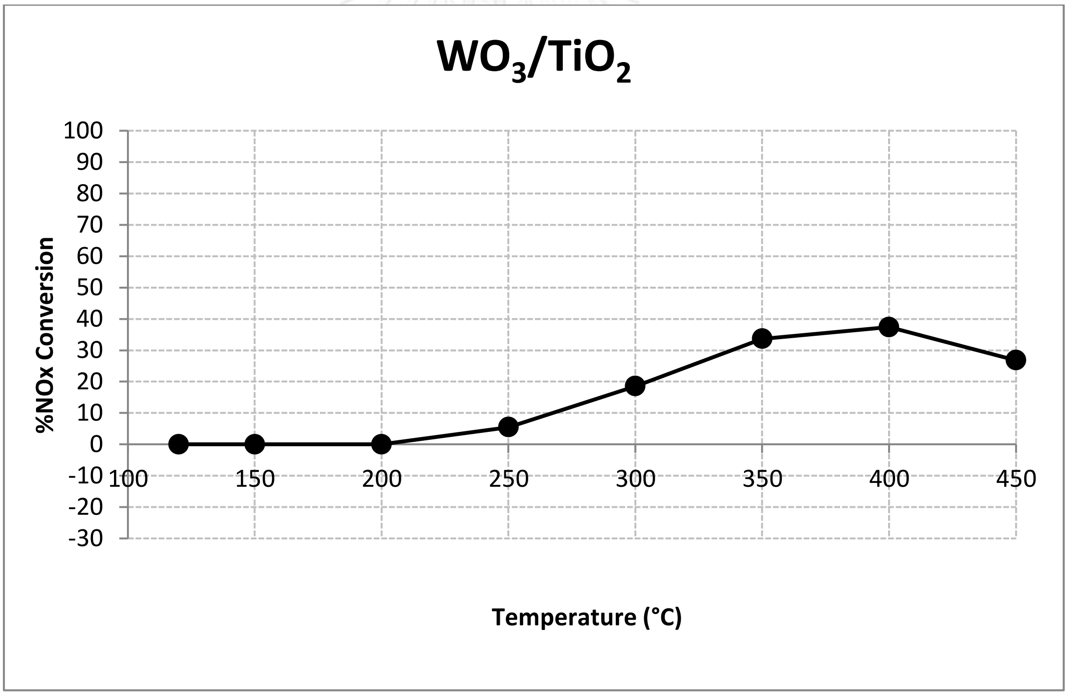

Figure 4.6 NOx conversion during the SCR reaction on WO_3/TiO_2 catalyst.

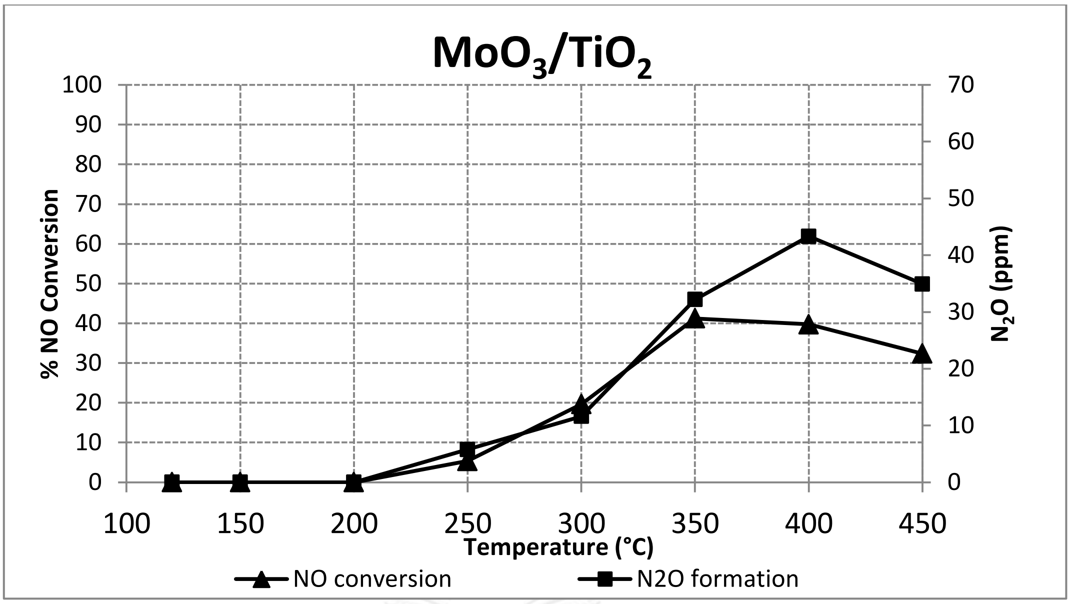

Figure 4.7 NO conversion and N_2O formation during the SCR reaction on MoO_3/TiO_2 catalyst.

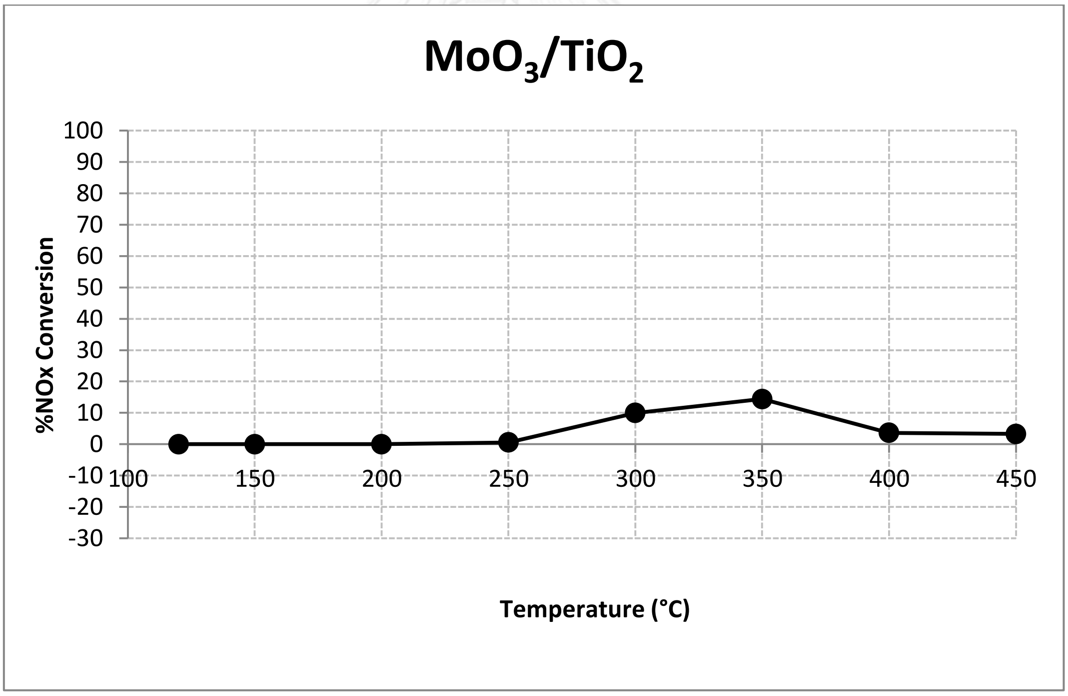

Figure 4.8 NOx conversion during the SCR reaction on MoO_3/TiO_2 catalyst

4.2.2.4 V_2O_5-WO_3/TiO_2

The results of SCR on V_2O_5-WO_3/TiO_2 catalyst are shown in Figures 4.9 and 4.10. For this catalyst, the reaction begins at a reaction temperature around 150 °C. NO conversion begins at 150 °C and increases until reaching a maximum, 100%, at 300 °C. When the reaction temperature is increased beyond 350 °C, however, NO conversion sharply drops to 26.15% at 400 °C. Since N_2O cannot be observed at any reaction temperature, NOx conversion profile showed in Figure 4.10 is the same profile with NO conversion profile showed in Figure 4.9.

4.2.2.5 V_2O_5-MoO_3/TiO_2

The results of SCR on MoO_3/TiO_2 catalyst are shown in Figures 4.11 and 4.12. For this catalyst, the reaction begins at a reaction temperature between 150-200 °C. NO conversion begins at 200 °C and increases until reaching a maximum, 50.13%, at 300 °C. Beyond this reaction temperature NO conversion rapidly decreases to around 17.3% at 350 °C and down to zero when the reaction temperature is in the range 400-450 °C

N_2O is firstly observed at reaction temperature 350 °C, 23.8 ppm. The concentration of N_2O increases to 28.2 ppm at 400 °C.

NOx conversion profile showed in Figure 4.11 is similar to NO conversion profile showed in Figure 4.12. The difference is in the reaction temperature region 350-450 °C where the values of NOx conversion are lower than the values of NO conversion in the temperature region. This is due to the formation of N_2O in that the reaction temperature region. The values of NOx conversion became negative in the reaction temperature region 350-350 °C because the amount of N_2O form is higher than the amount of NO eliminated.

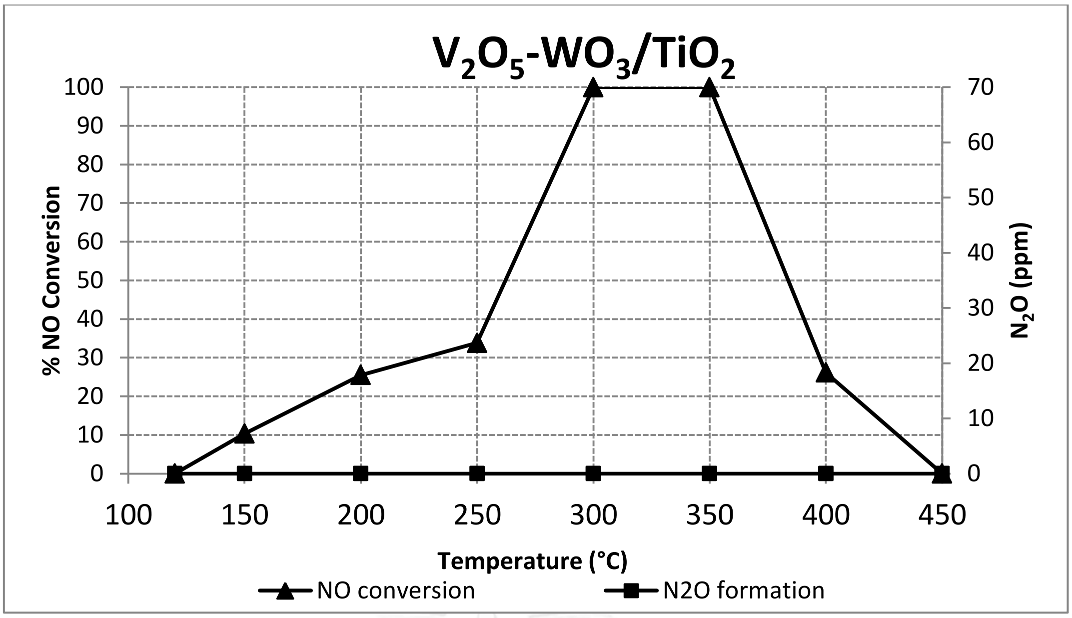

Figure 4.9 NO conversion and N_2O formation during the SCR reaction on V_2O_5-WO_3/TiO_2 catalyst.

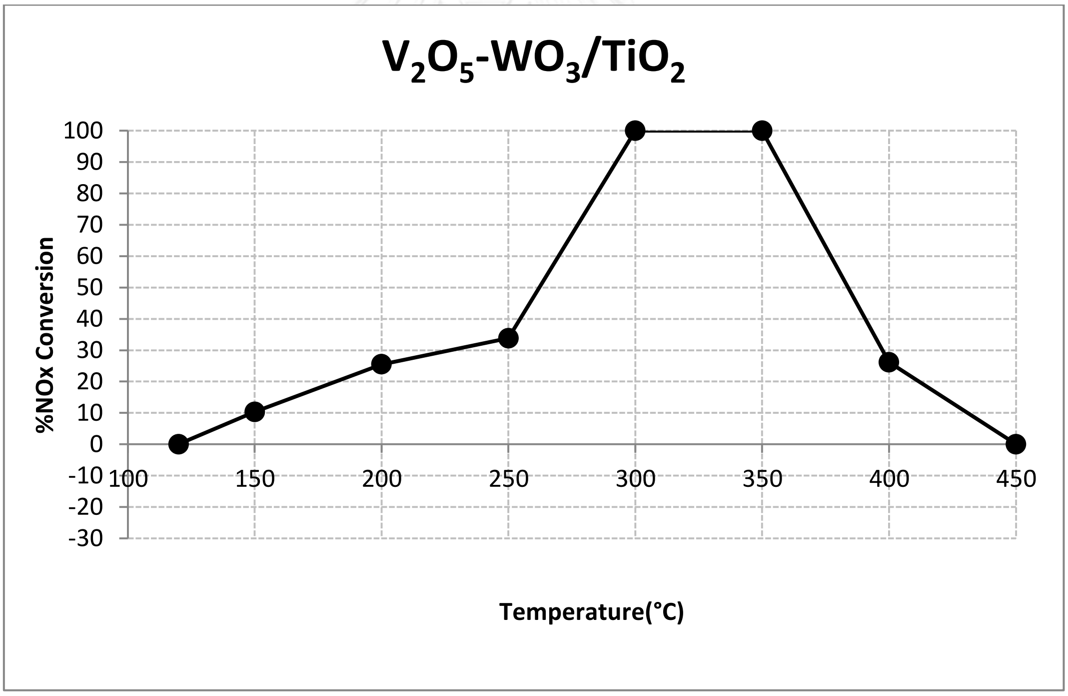

Figure 4.10 NOx conversion during the SCR reaction on V_2O_5-WO_3/TiO_2 catalyst.

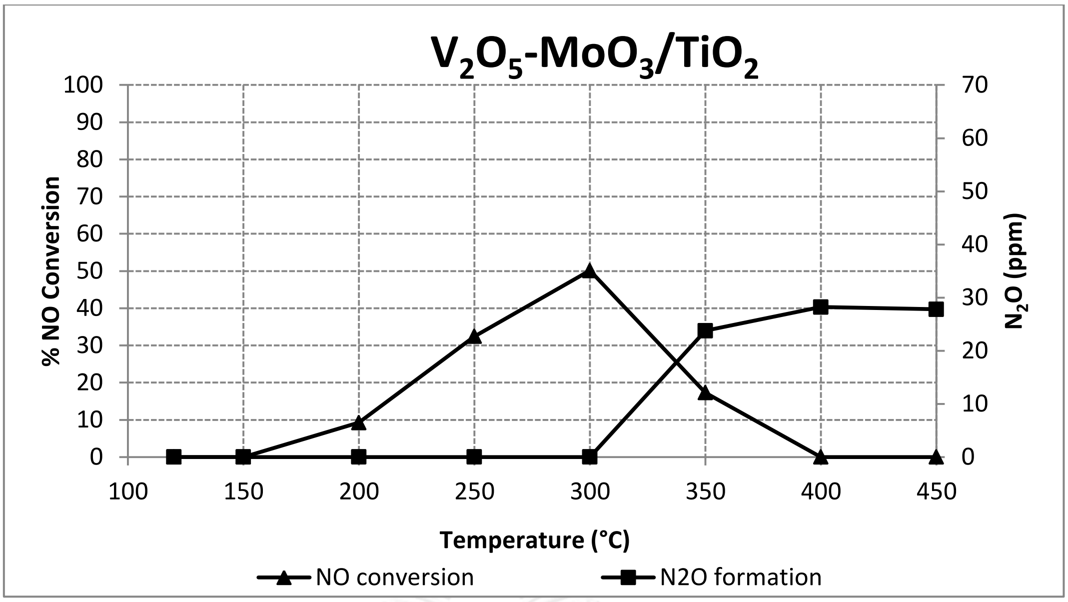

Figure 4.11 NO conversion and N_2O formation during the SCR reaction on V_2O_5-MoO_3/TiO_2 catalyst.

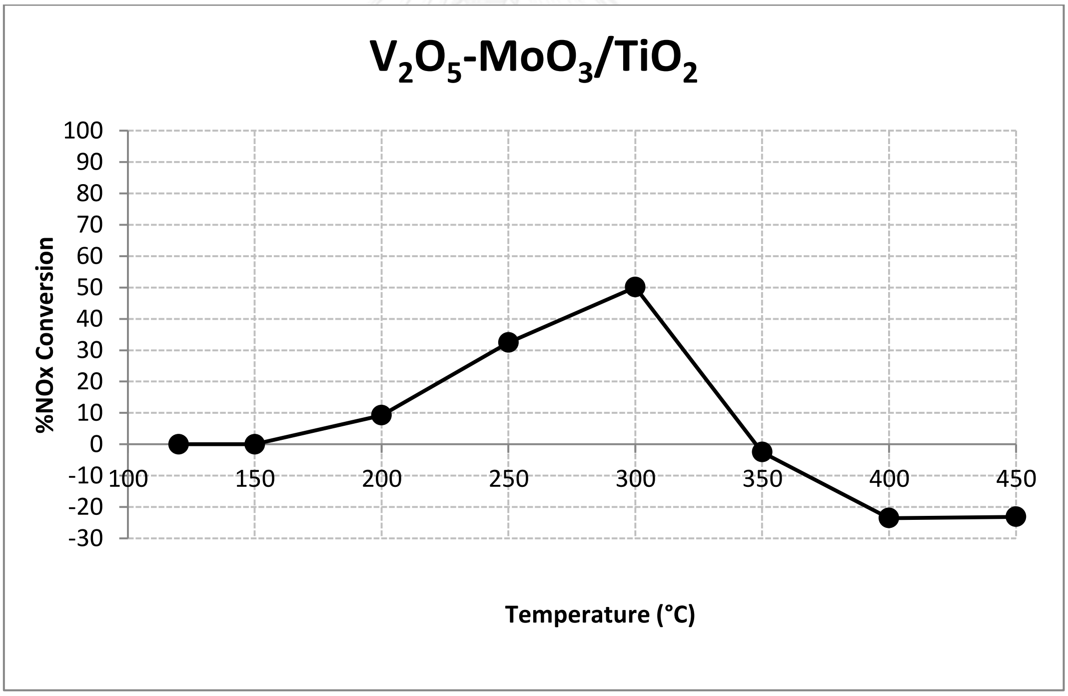

Figure 4.12 NOx conversion during the SCR reaction on V_2O_5-MoO_3/TiO_2 catalyst.

4.3 The effect of SO_2 on the SCR of NO by NH_3

The effect of SO_2 on the SCR of NO by NH_3 is studied by using gas composition containing 120 ppm of NO, 120 ppm of NH_3, 15 vol% of O_2, 15 vol% of H_2O and using N_2 as balancing gas. The total flow rate base on dry basis is 200 ml/min. This experiment is used for studying the effect of SO_2 on the SCR of NO and N_2O formation during the SCR process on V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts. The experimental results include NO conversion and N_2O formation.

4.3.1 V_2O_5/TiO_2

In Figure 4.13, NO conversion during the SCR reaction in the presence and absence of SO_2 on V_2O_5/TiO_2 catalyst begins at 150 °C. For the SCR reaction in the absence of SO_2, NO conversion slowly increases until reaching 100% at 250 °C and slowly decreases after 300 °C until became zero at 450°C. The SCR reaction in the presence of SO_2 has a maximum NO conversion, 54.1 %, at 300 °C. At the reaction temperature more than 350 °C, however, the SCR reaction in the presences of SO_2 has higher NO conversion than the SCR reaction in the absence of SO_2.

Effect of SO_2 on N_2O formation on V_2O_5/TiO_2 catalyst during the SCR reaction is shown in Figure 4.14. N_2O formation from the SCR reaction in the absences of SO_2 appears at 350 °C, faster than N_2O formation from the SCR reaction in the presence of SO_2 that appears at 400 °C. However concentration of N_2O form from both process are similar.

From the results, SO_2 decreases NO conversion in the SCR process over V_2O_5/TiO_2 catalyst when the reaction temperature is lower than 300 °C but increases NO conversion during the SCR process when the reaction temperature is higher than 300 °C. SO_2 does not change concentration of N_2O form during the SCR process when reaction temperature is lower than 450 °C on V_2O_5/TiO_2 catalyst.

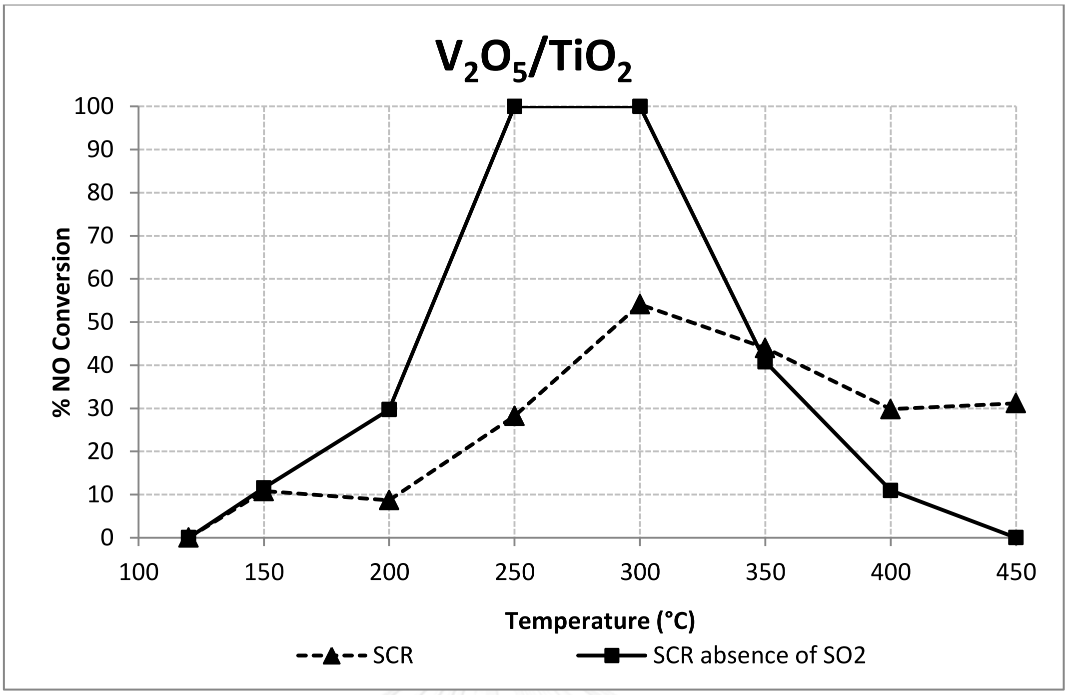

Figure 4.13 NO conversion during the SCR reaction in the absence and presence of SO_2 on V_2O_5/TiO_2 catalyst.

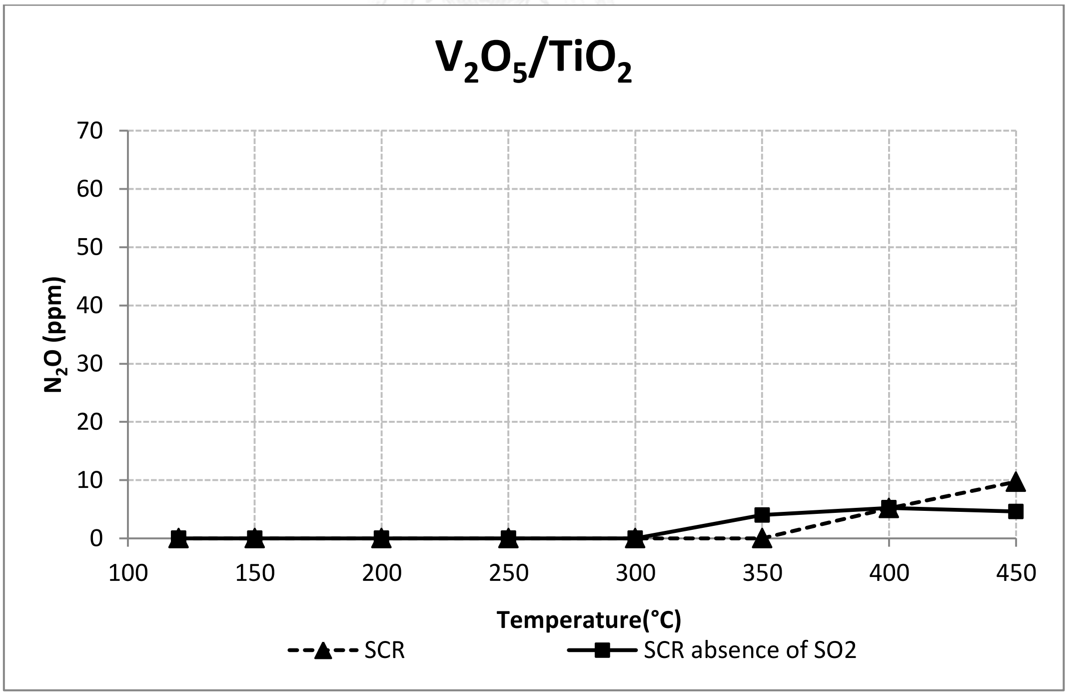

Figure 4.14 N_2O formation during the SCR reaction in the absence and presence of SO_2 on V_2O_5/TiO_2 catalyst.

4.3.2 WO_3/TiO_2

Behavior of WO_3/TiO_2 catalyst during the SCR process in absence and the presence of SO_2 differs from the behavior of V_2O_5/TiO_2 catalyst. NO conversion curves in Figure 4.15 from the SCR process in the absence and presence of SO_2 on WO_3/TiO_2 are similar. NO conversion from the SCR in the absence of SO_2 on V_2O_5/TiO_2 catalyst is higher than NO conversion from the SCR in the absence of SO_2 on WO_3/TiO_2 catalyst. V_2O_5/TiO_2 catalyst, however, is more sensitive to the SCR in the presence SO_2 than WO_3/TiO_2 catalyst. NO conversion from the SCR reaction in the absence of SO_2 slowly increases until reaching 34.8% at 400 °C and slowly decreases after that. The SCR reaction in the presence of SO_2 has a maximum NO conversion, 37.4%, at 400 °C. At the reaction temperature 450 °C, however, the SCR reaction in the presences of SO_2 has higher NO conversion than the SCR reaction in the absence of SO_2.

Effect of SO_2 on N_2O formation on WO_3/TiO_2 catalyst in SCR is shown in Figure 4.16. N_2O formation behavior in the SCR on WO_3/TiO_2 catalyst is different from NO conversion behavior during the SCR reaction on WO_3/TiO_2 catalyst. N_2O formed from the SCR reaction in the absence of SO_2 begins at 300 °C while the SCR reaction in the presence of SO_2 does not produce N_2O. N_2O formation in the SCR process is sensitive to SO_2 more than NO conversion.

From the results, SO_2 does not have any observable effect on NO conversion in the SCR process on WO_3/TiO_2 catalyst at the reaction temperature less than 400 °C but increases NO conversion in the SCR process when the reaction temperature is higher than 450 °C. The presence of SO_2 inhibits the formation of N_2O over WO_3/TiO_2 catalyst.

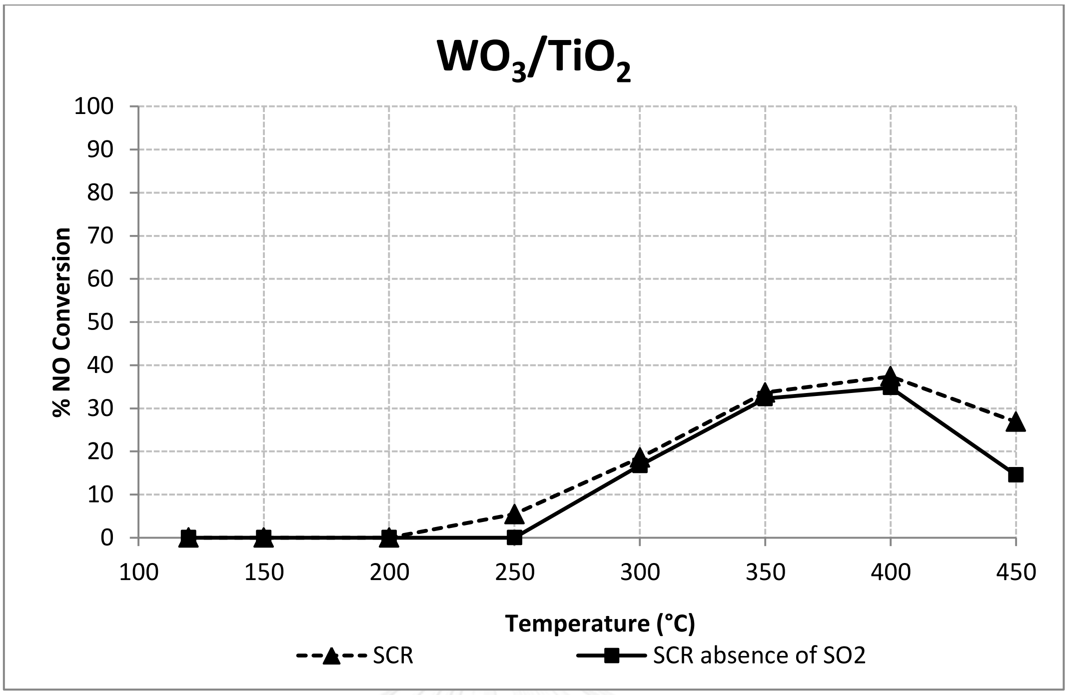

Figure 4.15 NO conversion during the SCR reaction in the absence and presence of SO_2 on WO_3/TiO_2 catalyst.

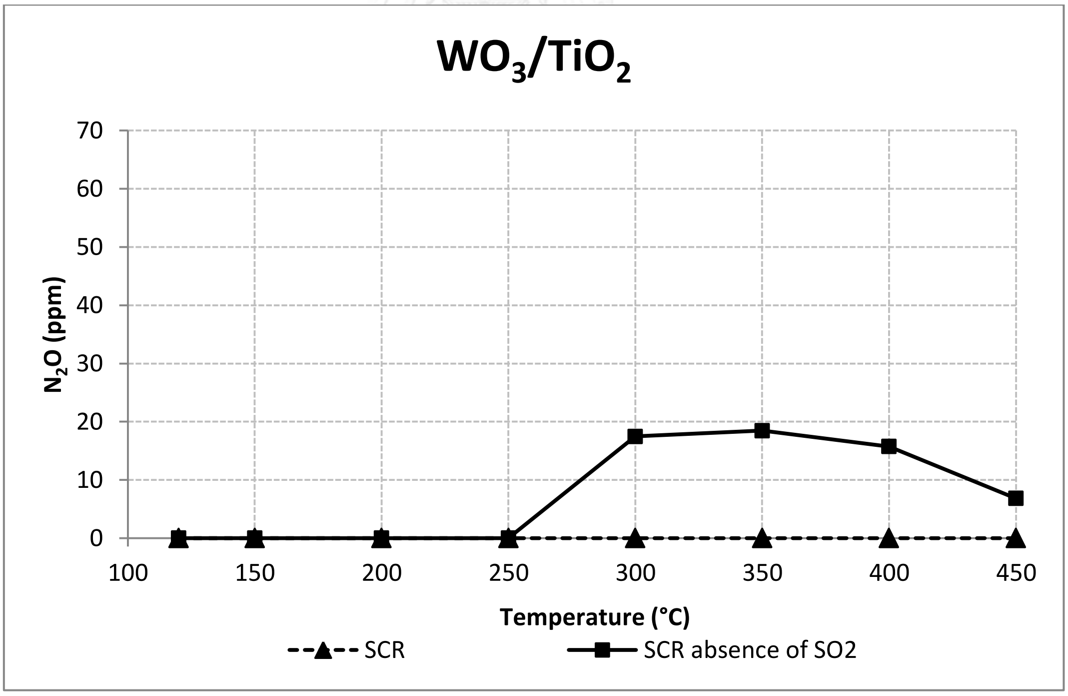

Figure 4.16 N_2O formation during the SCR reaction in the absence and presence of SO_2 on WO_3/TiO_2 catalyst.

4.3.3 MoO_3/TiO_2

NO conversions from the SCR in the absence and the presence of SO_2 in Figure 4.17 begin at the same the reaction temperature, 250 °C. For the SCR process in the absence of SO_2, NO conversion slowly increases until reaching 40.31% at 400 °C and rapidly decreases after that. The SCR process in the presence of SO_2 has a maximum NO conversion, 41.23% at 350°C and slowly decreases after that temperature. In the SCR process in the presence of SO_2, this catalyst has NO conversion curve similar to that of WO_3/TiO_2 catalyst. But the behavior of MoO_3/TiO_2 catalyst in the SCR in the absence of SO_2 is difference from WO_3/TiO_2 catalyst. NO conversion over WO_3/TiO_2 catalyst is higher than the conversion over MoO_3/TiO_2 catalyst at 350 °C.

Effect of SO_2 on N_2O formation on MoO_3/TiO_2 catalyst in SCR is shown in Figure 4.18. N_2O formation behavior on MoO_3/TiO_2 catalyst is sensitive to SO_2 in the reactant gas. Effect of SO_2 on N_2O formation behavior on MoO_3/TiO_2 catalyst differs from WoO_3/TiO_2 catalyst. The amount of N_2O formed from the SCR reaction in absence of SO_2 is higher than the amount of N_2O formed from the SCR reaction in the presence of SO_2. N_2O formed from the SCR reaction in the absences and the presence of SO_2 at the same the reaction temperature, 300 °C.

From the results, SO_2 increases NO conversion in the SCR process over MoO_3/TiO_2 catalyst at the reaction temperature less than 350 °C and higher than 450 °C. The presence of SO_2 produces a large amount of N_2O form from the SCR process on MoO_3/TiO_2 catalyst.

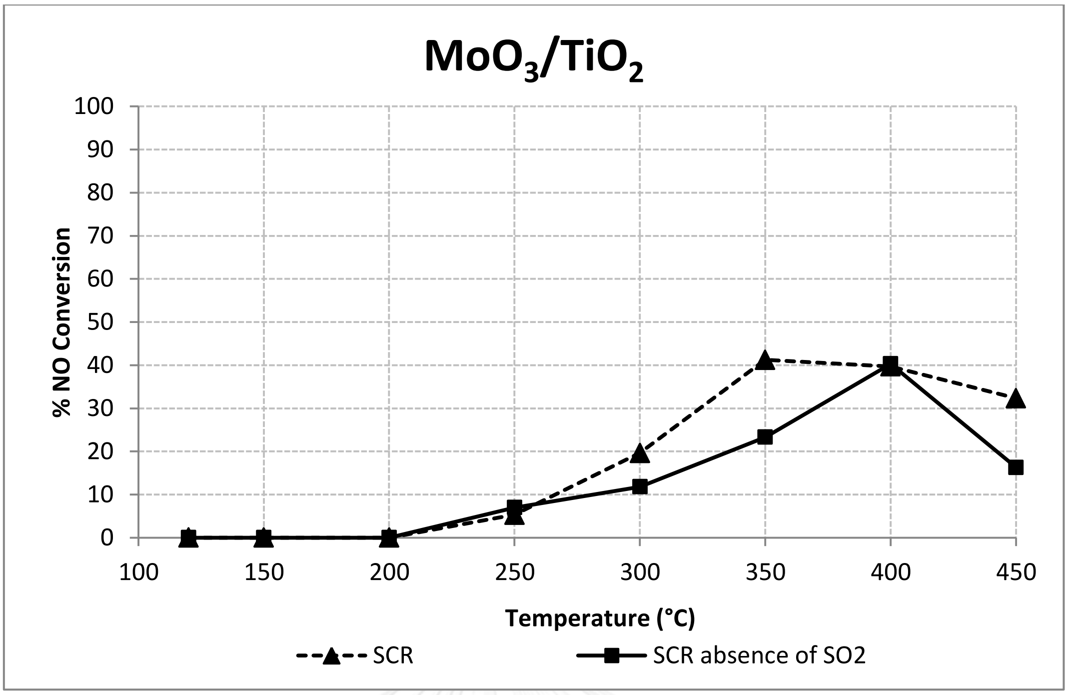

Figure 4.17 NO conversion during the SCR reaction in the absence and presence of SO_2 on MoO_3/TiO_2 catalyst.

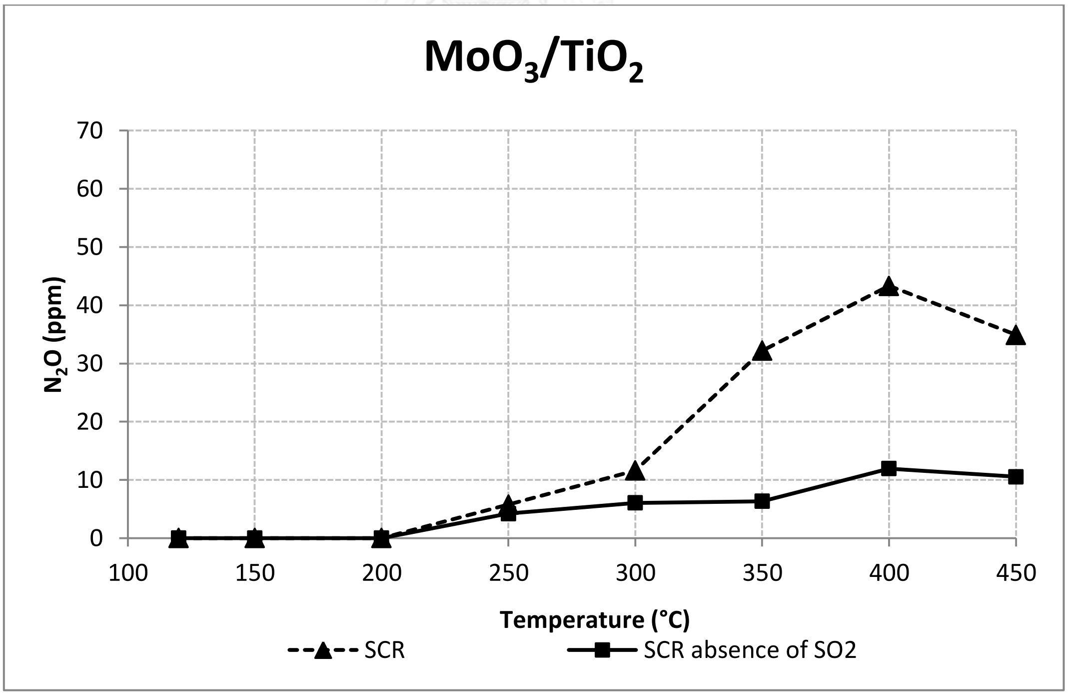

Figure 4.18 N_2O formation during the SCR reaction in the absence and presence of SO_2 on MoO_3/TiO_2 catalyst.

4.3.4 V_2O_5-WO_3/TiO_2

V_2O_5-WO_3/TiO_2 catalyst works well in wider reaction temperature than V_2O_5/TiO_2 or WO_3/TiO_2. NO conversion curves from the SCR in the absence and the presence of SO_2 on V_2O_5-WO_3/TiO_2 showed in Figure 4.19 are similar. NO conversion from both SCR conditions begins at the same the reaction temperature, 150 °C. For the SCR reaction in the absence of SO_2, NO conversion increases until reaching 100% at 300-350 °C and sharply decreases to zero at 450 °C. The SCR reaction in the presence of SO_2 has maximum NO conversion, 100% at 200°C and slowly decrease to zero at 450 °C.

In Figure 4.20, V_2O_5-WO_3/TiO_2 catalyst is not sensitive to SO_2 on the SCR process because N_2O does not form from the SCR process in the presence and absence of SO_2 conditions.

From the described results, SO_2 increases NO conversion in the SCR process on V_2O_5-WO_3/TiO_2 catalyst when the reaction temperature is lower than 150 °C but decreases NO conversion in the SCR process when the reaction temperature is lower than 350°C. SO_2 does not have observable effect on N_2O formed from the SCR on V_2O_5-WO_3/TiO_2 catalyst.

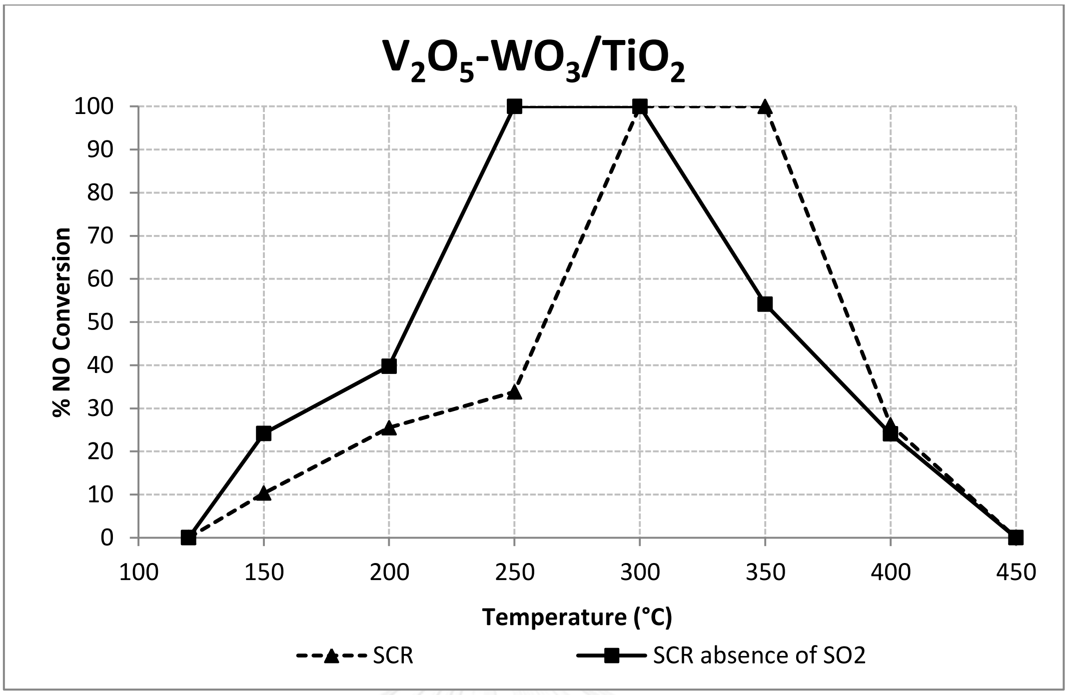

Figure 4.19 NO conversion during the SCR reaction in the absence and presence of SO_2 on V_2O_5-WO_3/TiO_2 catalyst.

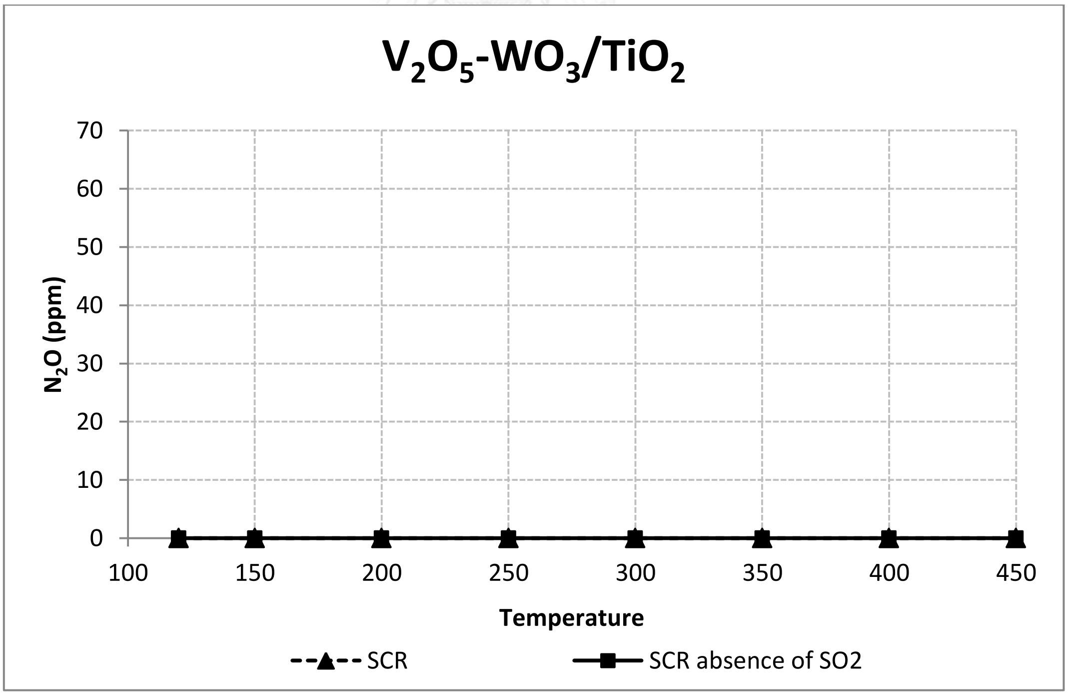

Figure 4.20 N_2O formation during the SCR reaction in the absence and presence of SO_2 on V_2O_5-WO_3/TiO_2 catalyst.

4.3.5 V_2O_5-MoO_3/TiO_2

The behavior of V_2O_5-MoO_3/TiO_2 catalyst differs from the behavior of V_2O_5-WO_3/TiO_2 catalyst. NO conversion over V_2O_5-MoO_3/TiO_2 catalyst in the SCR process in the absence of SO_2 is lower than NO conversion of V_2O_5-WO_3/TiO_2 catalyst during the SCR reaction in the absence of SO_2. This catalyst does not sensitive to SO_2 in the SCR process. NO conversion curves in Figure 4.21 from the SCR reaction in the absence and presence of SO_2 are similar. NO conversion from the SCR reaction in the presence and absence of SO_2 begin at the same reaction temperature, 200 °C. NO conversion from the SCR reaction in absence of SO_2 increases until reaching 49.73%, at 300 °C and slowly decreases to zero, at 450 °C. The SCR reaction in the presence of SO_2 has a maximum NO conversion, 50.13%, at 300 °C and slowly decreases to zero at 400 °C.

Effect of SO_2 on N_2O formation on V_2O_5-MoO_3/TiO_2 catalyst in SCR is shown in Figure 4.22. N_2O formation behavior of V_2O_5-MoO_3/TiO_2 catalyst is similar to V_2O_5-WO_3/TiO_2 catalyst. N_2O formation behavior of this catalyst is not sensitive to SO_2 on the SCR process. N_2O in both conditions appears at 350 °C and the amount of N_2O formed are about the same.

From the results, SO_2 does not have significant effect on NO conversion in the SCR process at the reaction temperature lower than 350°C but decreases NO conversion in the SCR process at the reaction temperature higher than 400 °C. In the other ways, SO_2 does not have effect on N_2O formation from the SCR process in V_2O_5-MoO_3/TiO_2 catalyst.

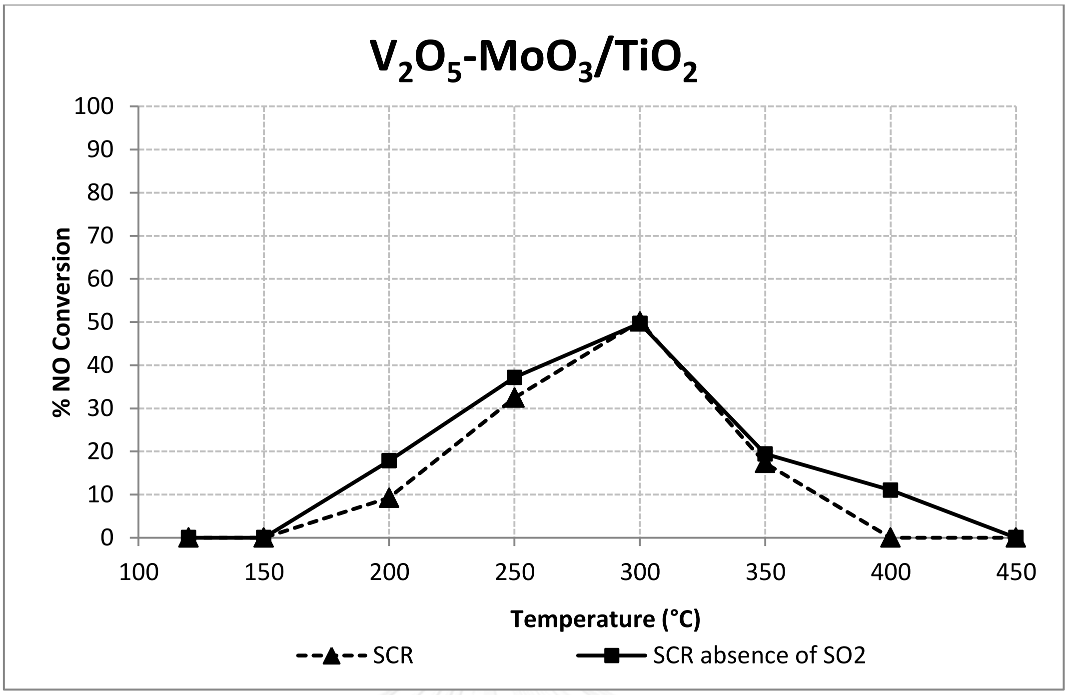

Figure 4.21 NO conversion during the SCR reaction in the absence and presence of SO_2 on V_2O_5-MoO_3/TiO_2 catalyst.

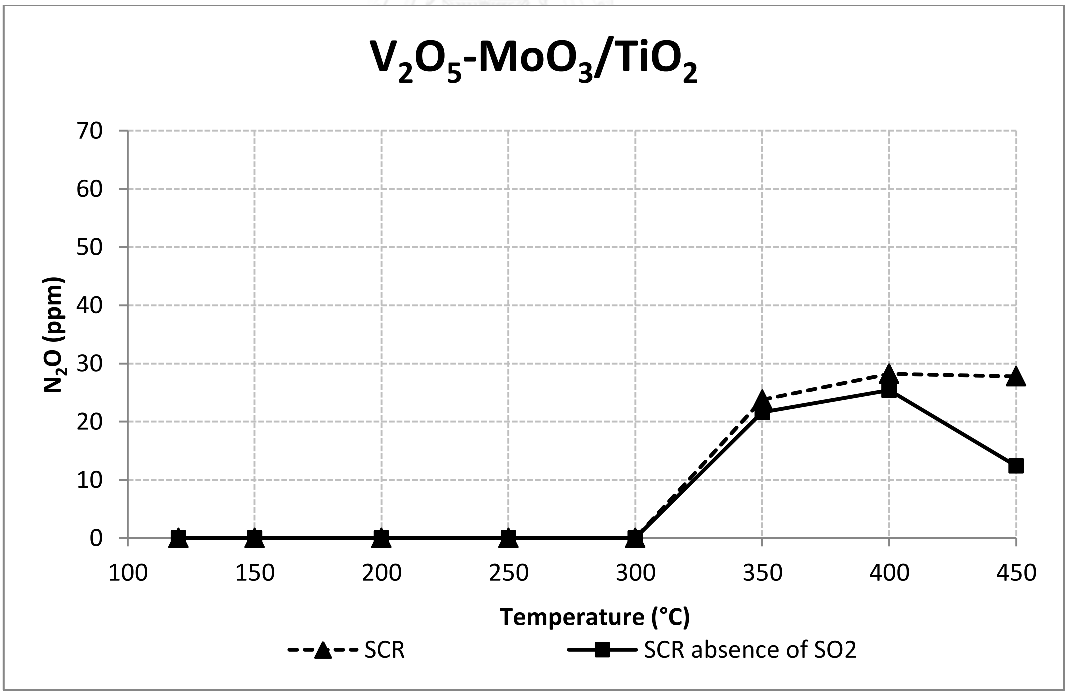

Figure 4.22 N_2O formation during the SCR reaction in the absence and presence of SO_2 on V_2O_5-MoO_3/TiO_2 catalyst.

4.3.6 The effect of SO_2 on the SCR of NO by NH_3

SO_2 is normally present in fuel gases of the SCR process. The effect of SO_2, therefore, is a topic of study in the research. The experimental results show that the presence of SO_2 in the feed gas can increase NO conversion in the SCR process over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2 and V_2O_5-WO_3/TiO_2 catalysts, at high reaction temperature i.e. higher than 350 °C.

During the SCR processes, two main reactions usually occur. The first one is the SCR reaction which leads the reduction of NO in the effluent gas. This reaction can occurs at any operating temperature. The second reaction is the oxidation of NH_3. The latter reaction leads to the formation of NO which results in increasing NO concentration in the effluent gas. The oxidation of NH_3, however, requires higher reaction temperature to initiate, typically higher than 300 °C. The presence of SO_2 affects both reaction which results in NO conversion profile changing at different reaction temperature.

Before SO_2 adsorption

After SO_2 adsorption

Figure 4.23 Catalyst structure before and after SO_2 adsorption.

When SO_2 presences in the reaction gas, SO_2 can adsorbs on the catalyst surface. The adsorption of SO_2 blocks a Lewis acidic site but produces two Brønsted acid sites (see Figure 4.23). From the model the decrease amount of Lewis acidic site should relate to the changing in NO conversion and the oxidation of NH_3. That is both the SCR reaction of NO by NH_3 and the oxidation of NH_3 should begin with the adsorption of NH_3 on Lewis acid site. The blocking of Lewis acid site leads to the decreases in NO conversion at low reaction temperature. At high reaction temperature, the blocking leads to both the reduction of the SCR reaction and the oxidation of NH_3. But the effect on the oxidation of NH_3 is larger, the overall NO conversion at high reaction temperature increases.

The results show that on V_2O_5/TiO_2, $WO_3/\ TiO_2$, $MoO_3/\ TiO_2$ and V_2O_5-$WO_3/\ TiO_2$ catalyst, SO_2 affects to increases NO conversion in the SCR process at high temperature. The results can demonstrate that at high temperature, NH_3 adsorption on the catalyst surface is enhanced by SO_2. SO_2 in the SCR process increases the number of Brønsted acid sites on the catalyst surface [52]. But in the different way, SO_2 in the SCR process decreases the amount of Lewis acid sites on the catalyst.

In the absence of SO_2, Lewis acid sites open to NH_3 molecules in the gas phase. In the presence of SO_2 Lewis acid sites are blocked by the absorbed of SO_2. One Lewis acid site was blocked but two Brønsted acid sites occurred instead. Since NH_3 oxidation decrease when SO_2 present in the fuel gas, Lewis acid sites are the sites when NH_3 oxidation occur.

N_2O formation is similar to NO conversion. N_2O formation increases in the SCR process on V_2O_5/TiO_2, $MoO_3/\ TiO_2$, and V_2O_5-$MoO_3/\ TiO_2$ catalyst at high temperature. The results support the above assumption that SO_2 have decrease the SCR of NO by NH_3 and decrease NH_3 oxidation at high temperature.

4.4 The effect of O_2 on the SCR reaction of NO by NH_3.

The effect of O_2 on the SCR reaction of NO by NH_3 is studied by using gas reactant containing 120 ppm of NO, 120 ppm of NH_3, 30 ppm of SO_2, 15 vol% of H_2O and using N_2 as balancing gas. The total flow rate base on dry basis is 200 ml/min. This experiment is used for studying the effect of O_2 on the SCR reaction of NO and N_2O formation during the SCR process on V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts. The experimental results include NO conversion and N_2O formation.

4.4.1 V_2O_5/TiO_2

The behavior of V_2O_5/TiO_2 on the SCR reaction is sensitive to the absence of O_2. In Figure 4.24, NO conversion of the SCR reaction in the presence and the absence of O_2 over V_2O_5/TiO_2 catalyst begins at different the reaction temperature. At the reaction temperature less than 350 °C, the SCR reaction in the absence of O_2 cannot eliminate NO. For the SCR reaction in the absence of O_2, NO conversion begins at a reaction temperature around 400 °C and increases until reaching 44.84%, at 450 °C. NO conversion during the SCR reaction in the presence of O_2 begins at 150 °C and has maximum NO conversion, 54.10%, at 300 °C.

Effect of O_2 on N_2O formation on V_2O_5/TiO_2 catalyst in SCR is shown in Figure 4.25. N_2O formation behavior of this catalyst is sensitive to the absence of O_2 too. This catalyst does not produce N_2O during the SCR reaction in the absence of O_2.

The results show that O_2 has effect to increases NO conversion in the SCR process at the reaction temperature less than 400 °C. O_2 has effect to increases N_2O formed on this catalyst in the SCR process.

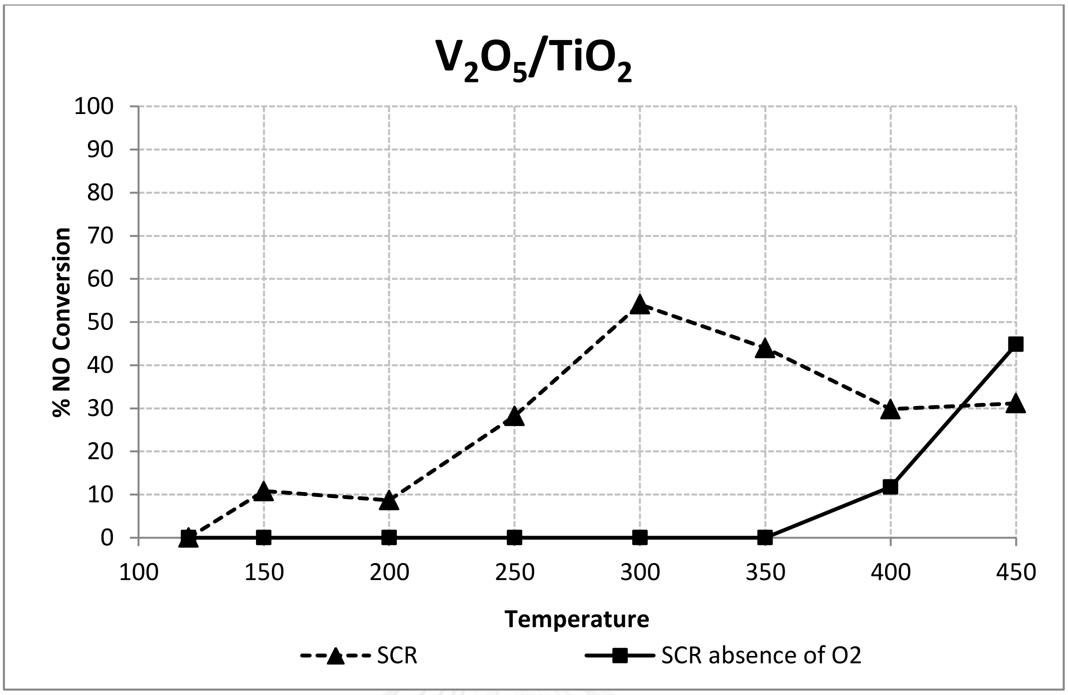

Figure 4.24 NO conversion during the SCR reaction in the absence and presence of O_2 on V_2O_5/TiO_2 catalyst.

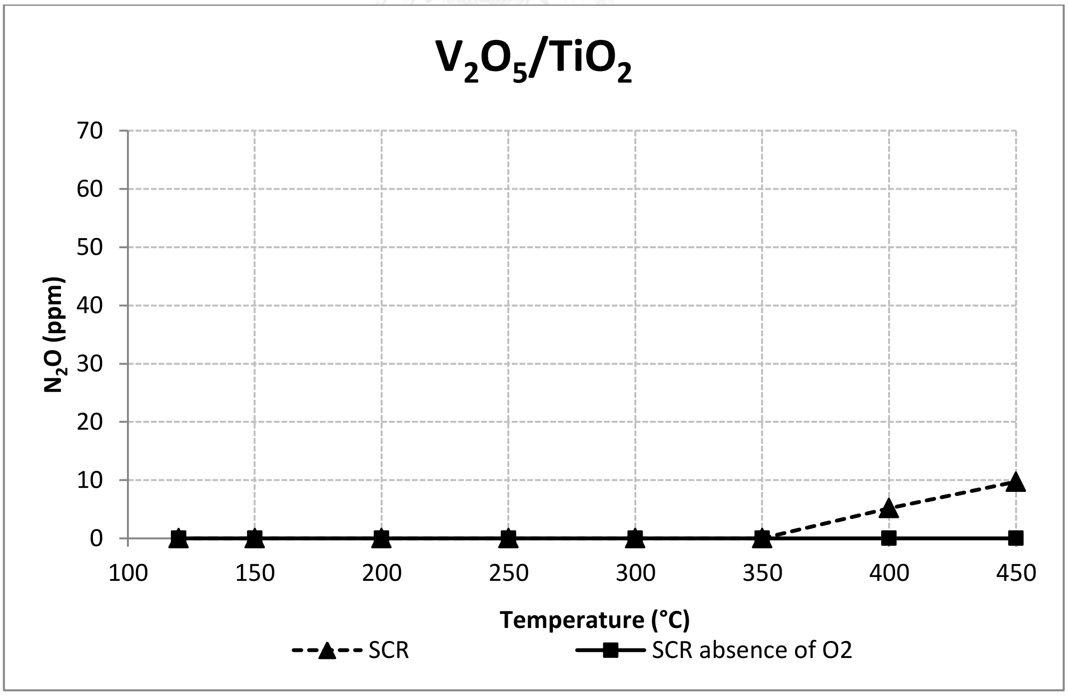

Figure 4.25 N_2O formation during the SCR reaction in the absence and presence of O_2 on V_2O_5/TiO_2 catalyst.

4.4.2 WO_3/TiO_2

The behavior of WO_3/TiO_2 catalyst in the SCR reaction in the absence and the presence of O_2 different from V_2O_5/TiO_2 catalyst. NO conversion curves are shown in Figure 4.26. The behavior of WO_3/TiO_2 catalyst is sensitive to O_2 containing in the SCR process. This catalyst cannot reduce NO from the reactant gas in the absence of O_2 while NO conversion on V_2O_5/TiO_2 catalyst begins at 400 °C from the SCR in the absence of O_2 process.

Effect of O_2 on N_2O formation on WO_3/TiO_2 catalyst in the SCR reaction is showed in Figure 4.27. N_2O formation on this catalyst during the SCR reaction in the presence and absence of O_2 are similar. N_2O does not form from the SCR in the presence of O_2. A small amount of N_2O forms from the SCR reaction in the absence of O_2 at 300 °C.

From the results, O_2 has effect on the SCR performance of this catalyst. O_2 increases NO conversion from the SCR process on this catalyst. The absence of O_2 inhibits the formation of N_2O over WO_3/TiO_2 catalyst.

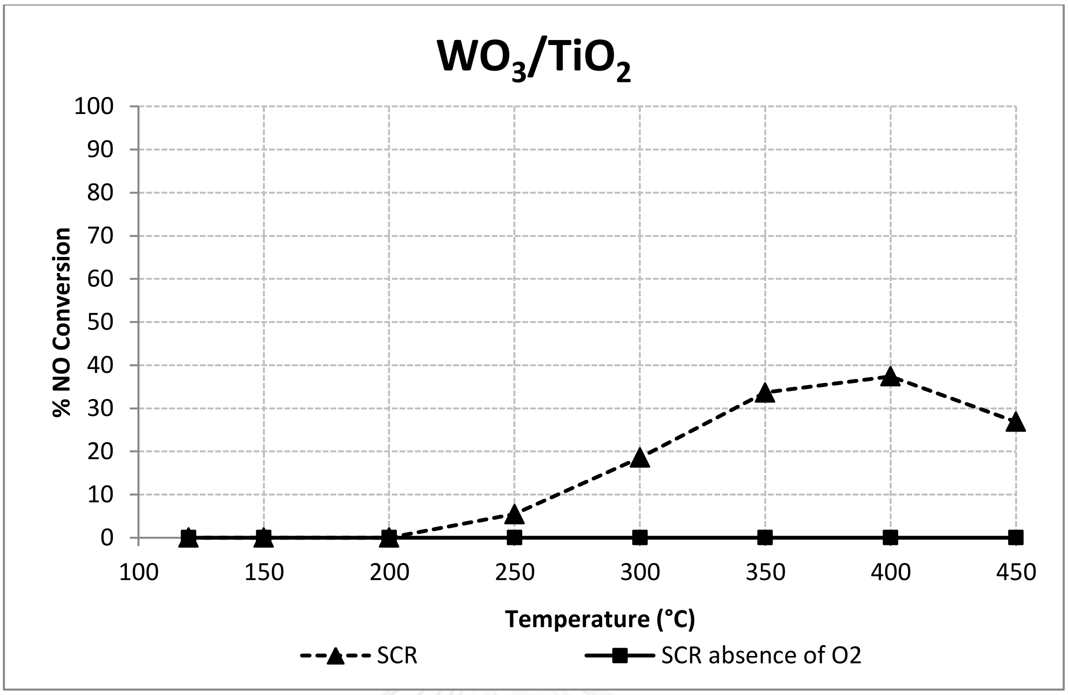

Figure 4.26 NO conversion during the SCR reaction in the absence and presence of O_2 on WO_3/TiO_2 catalyst.

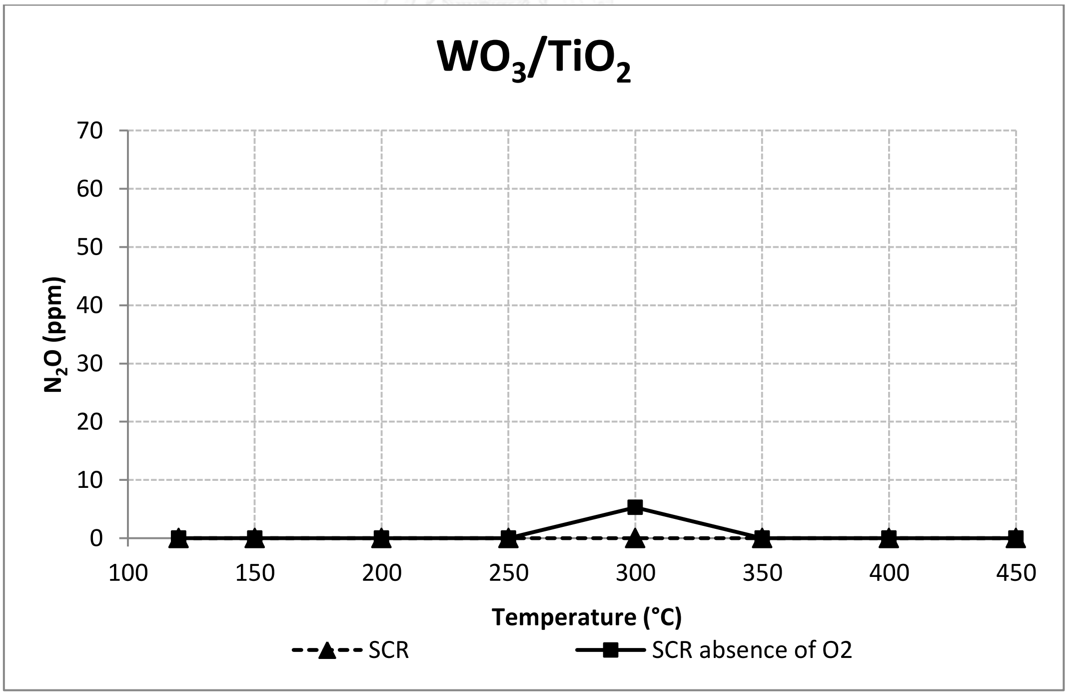

Figure 4.27 N_2O formation during the SCR reaction in the absence and presence of O_2 on WO_3/TiO_2 catalyst.

4.4.3 MoO_3/TiO_2

Behavior of MoO_3/TiO_2 in Figure 4.28 is different from the behavior of WO_2/TiO_2. NO conversion from the SCR in the absence of O_2 on MoO_3/TiO_2 catalyst begins at the reaction temperature more than 300 °C while NO conversion from the SCR reaction in the absence of O_2 on WO_3/TiO_2 catalyst is zero in every reaction temperature. The results indicate that MoO_3/TiO_2 catalyst is sensitive to the presence of O_2 on the SCR process. NO conversion from the SCR reaction in the absence of O_2 begins at 350 °C and slowly reaching 48.09%, at 450°C. NO conversion from the SCR in the presence of O_2 increases at 250 °C and reaching a maximum value 41.23%, at 350°C.

Effect of O_2 on N_2O formation on MoO_3/TiO_2 catalyst in the SCR reaction is shown in Figure 4.29. N_2O formation behavior of MoO_3/TiO_2 catalyst is sensitive to the presence/absence of O_2 in the SCR reaction too. Effect of O_2 on N_2O formation behavior of MoO_3/TiO_2 catalyst is differs from WO_3/TiO_2 catalyst. A small amount of N_2O forms from the SCR in the absence of O_2 on WO_3/TiO_2. N_2O formed from the SCR reaction in the absence of O_2 on MoO_3/TiO_2 catalyst is higher than N_2O formed from the SCR in the presence of O_2 at reaction temperature less than 450 °C. However, N_2O formed from the SCR reaction in the absence of O_2 is less than N_2O form from the SCR in the presence of O_2 at 450°C.

From the results, O_2 increases NO conversion in the SCR process over MoO_3/TiO_2 catalyst at any reaction temperature lower than 400 °C. O_2 decrease the amount of N_2O formed from the SCR reaction over MoO_3/TiO_2 catalyst when the reaction temperature is lower than 400 °C.

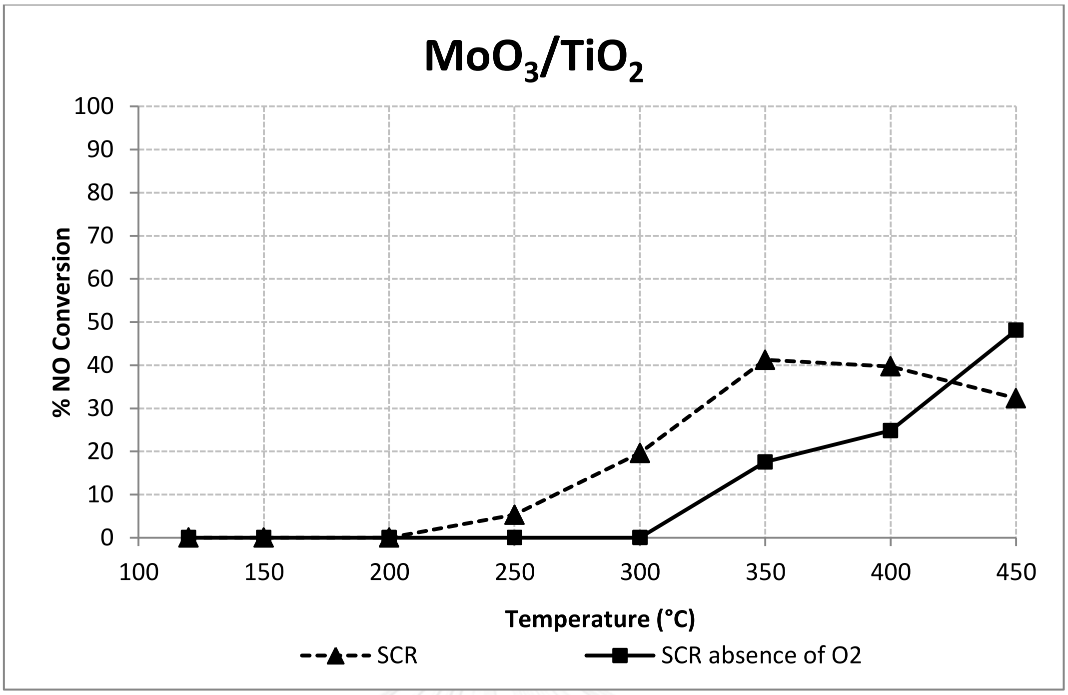

Figure 4.28 NO conversion during the SCR reaction in the absence and presence of O_2 on MoO_3/TiO_2 catalyst.

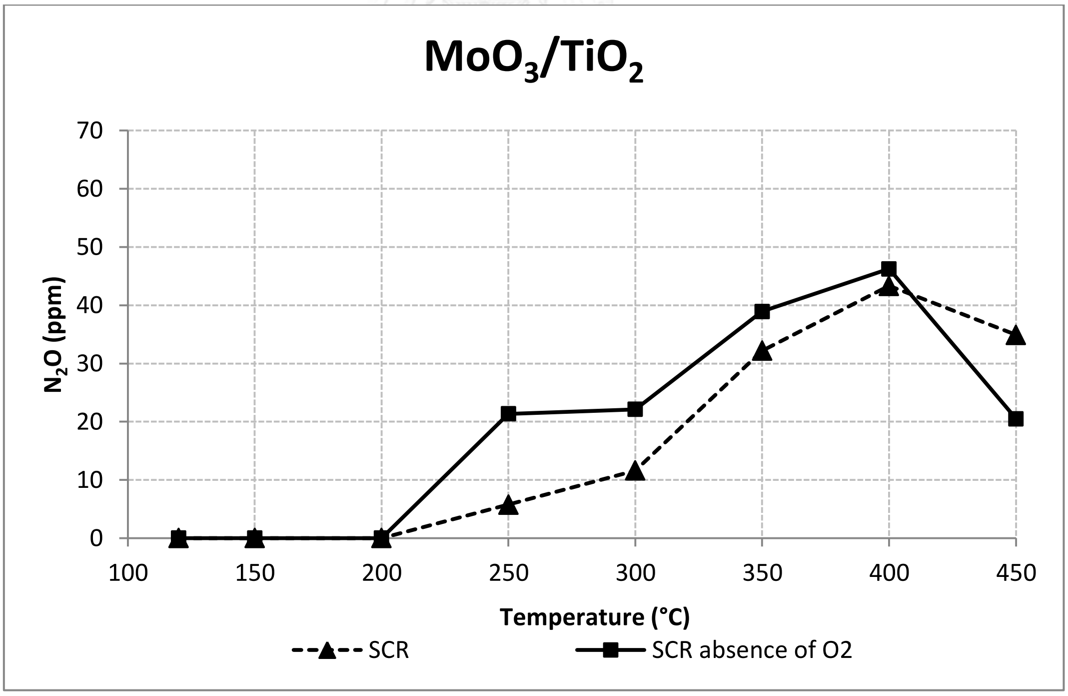

Figure 4.29 N_2O formation during the SCR reaction in the absence and presence of O_2 on MoO_3/TiO_2 catalyst.

4.4.4 V_2O_5-WO_3/TiO_2

The behavior of V_2O_5-WO_3/TiO_2 is sensitive to O_2 in the SCR process. NO conversion curves from the SCR reaction in the absence and presence of O_2 on V_2O_5-WO_3/TiO_2 showed in Figure 4.30 are different. NO conversion from the SCR in the absence of O_2 begins at 400 °C and sharply increases until reaching 67.08%, at 450 °C. NO conversion from the SCR reaction in the presence of O_2 begins at 150 °C and reaching the maximum 100%, at 300 °C.

From the results from V_2O_5-WO_3/TiO_2 catalyst showed in Figure 4.31, the N_2O formation behavior of V_2O_5-WO_3/TiO_2 is not sensitive to O_2 because this catalyst does not form N_2O from the SCR reaction in the presence and absence of O_2.

From the results, O_2 increases NO conversion in SCR process on V_2O_5-WO_3/TiO_2 catalyst. However, O_2 does not affect N_2O formation from the SCR on V_2O_5-WO_3/TiO_2 catalyst.

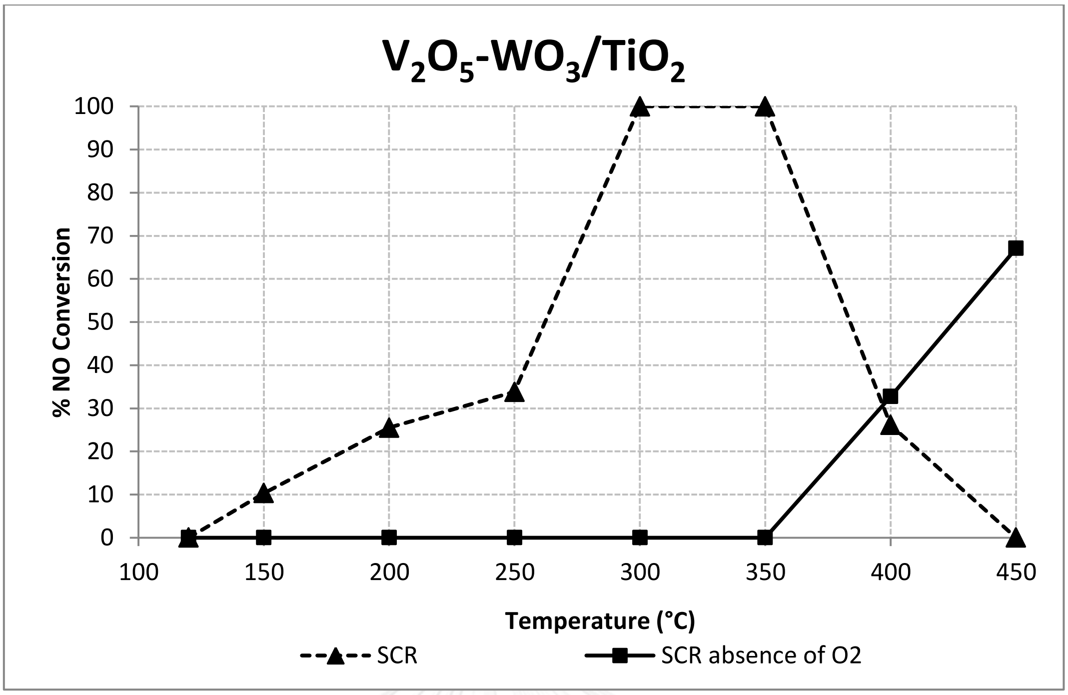

Figure 4.30 NO conversion during the SCR reaction in the absence and presence of O_2 on V_2O_5-WO_3/TiO_2 catalyst.

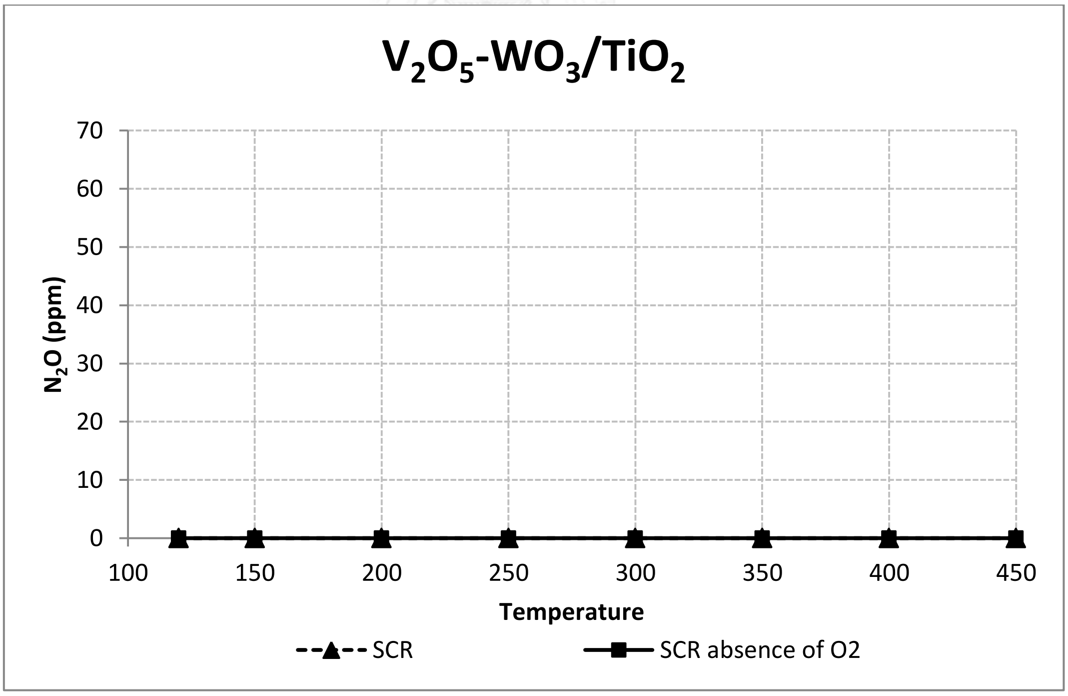

Figure 4.31 N_2O formation during the SCR reaction in the absence and presence of O_2 on V_2O_5-MoO_3/TiO_2 catalyst.

4.4.5 V_2O_5- MoO_3/TiO_2

The behavior of V_2O_5-MoO_3/TiO_2 catalyst is difference from the behavior of V_2O_5-WO_3/TiO_2 catalyst. NO conversion from the SCR in the absence of O_2 on V_2O_5-MoO_3/TiO_2 catalyst is less than NO conversion from the SCR in the absence of O_2 on V_2O_5-WO_3/TiO_2 catalyst. This catalyst is sensitive to O_2 in the SCR process. NO conversion curve in Figure 4.32 from the SCR in absence and presence of SO_2 are difference. NO conversion from SCR in the absence of O_2 begins at 250 °C and slowly increases reaching 57%, at 350 °C. NO conversion from the SCR in presence of O_2 begins at 200 °C and slowly decreases to zero at 400 °C.

Effect of O_2 on N_2O formation on V_2O_5-MoO_3/TiO_2 catalyst in the SCR process is shown in Figure 4.33. N_2O formation behavior of V_2O_5-MoO_3/TiO_2 catalyst differs from V_2O_5-WO_3/TiO_2 catalyst. N_2O formation behavior of V_2O_5-MoO_3/TiO_2 catalyst is sensitive to O_2 in the SCR process. But N_2O formation behavior of V_2O_5-WO_3/TiO_2 catalyst is not sensitive to O_2 in the SCR process. N_2O formed from the SCR reaction in the absence and the presence of O_2 on this catalyst are different. N_2O formed from the SCR reaction in the absence of O_2 on V_2O_5-MoO_3/TiO_2 catalyst begins at 350 °C. N_2O formed from the SCR reaction in the presence of O_2 on V_2O_5-MoO_3/TiO_2 catalyst begins at 250 °C. N_2O formed from the SCR reaction in the absence of O_2 on V_2O_5-MoO_3/TiO_2 is higher than N_2O formed from the SCR reaction in the presence of O_2 on V_2O_5-MoO_3/TiO_2.

From the results, O_2 have effect on NO conversion in the SCR process on this catalyst. O_2 increases NO conversion at the reaction temperature is lower than 300 °C. However, O_2 decreases NO conversion at the reaction temperature is higher than 350 °C. O_2 decreases N_2O formation from SCR process over V_2O_5-MoO_3/TiO_2 catalyst.

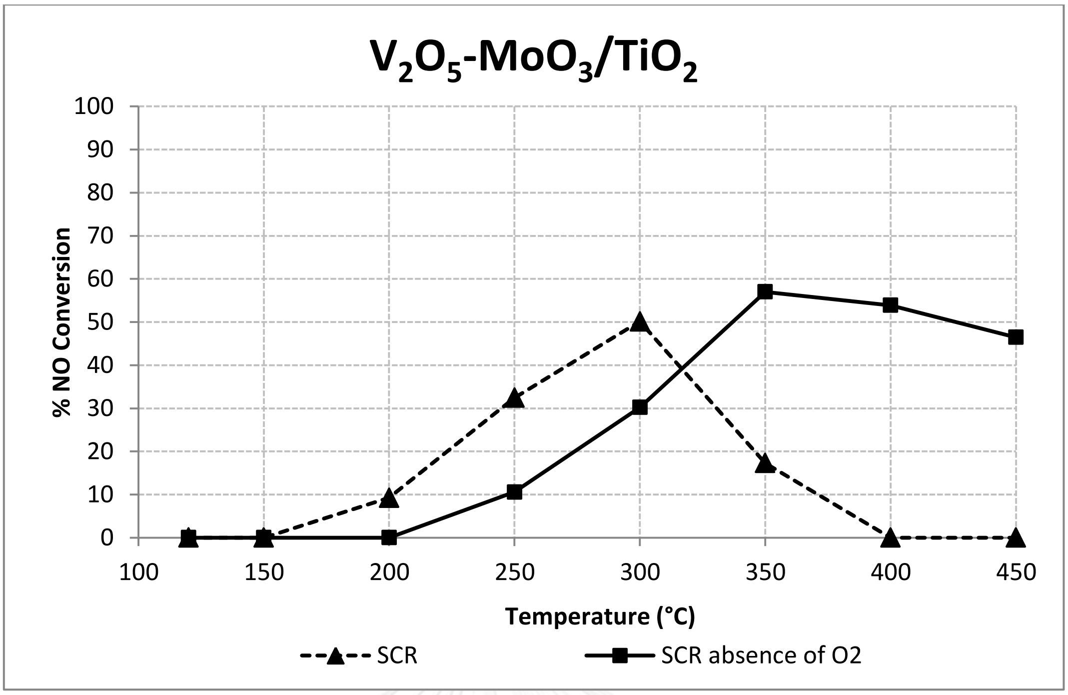

Figure 4.32 NO conversion during the SCR reaction in the absence and presence of O_2 on V_2O_5-WO_3/TiO_2 catalyst.

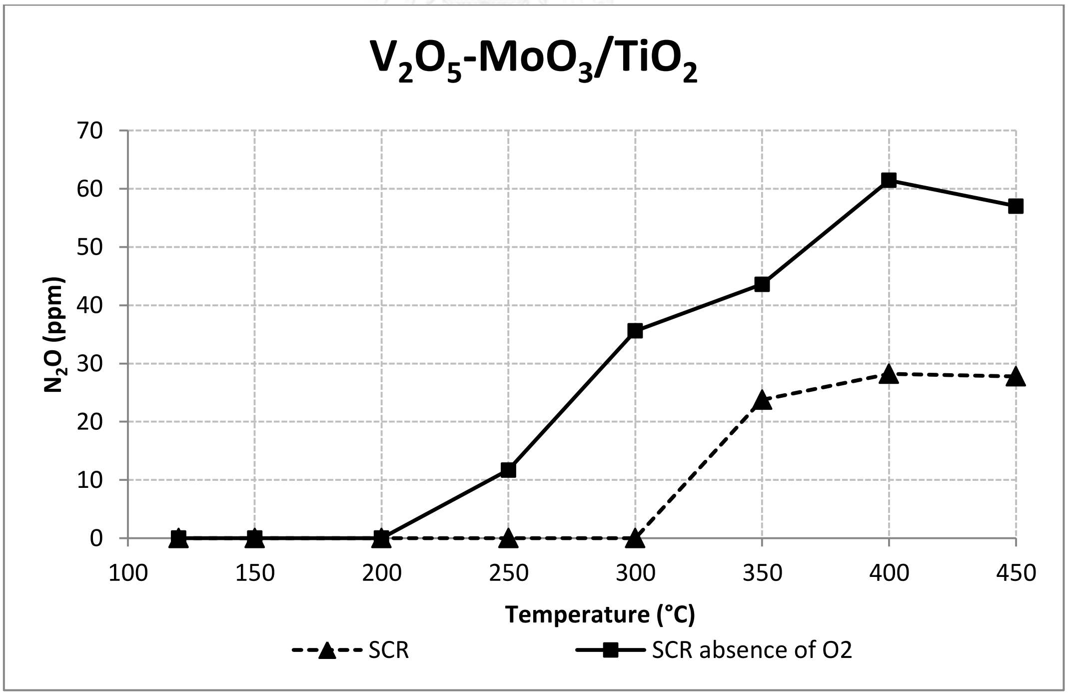

Figure 4.33 N_2O formation during the SCR reaction in the absence and presence of O_2 on V_2O_5-MoO_3/TiO_2 catalyst.

4.4.6 The effect of O_2 on the SCR of NO by NH_3 in the absence of O_2

The SCR of NO by NH_3 is the reaction between NO, NH_3, and oxygen in the process. The oxygen sources in the SCR experimental follow :

(i) Gases oxygen feed to the system
(ii) Lattice oxygen (oxygen anion) from catalyst surface
(iii) Oxygen impure in N_2 feed (99.999%)

Normally, O_2 in feed is mainly oxygen source in the SCR reaction in the presence of O_2. However, if O_2 feed was cut from the SCR reaction. The source of oxygen has only two sources remain, oxygen gas impurity from N_2 and oxygen anion from catalyst oxide on TiO_2 support.

From the SCR reaction in the absence of O_2 on V_2O_5, WO_3, MoO_3, V_2O_5-WO_3 and V_2O_5-MoO_3 catalysts on TiO_2 support, the results show that NO removable can occurs on V_2O_5/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalyst in the process at high temperature. However, WO_3/TiO_2 catalyst cannot remove NO in the SCR reaction in the absence of O_2. Oxygen source in the SCR reaction in the absence of O_2 might come from O_2 impurity in N_2 feed and metal oxide on catalysts. After observation at the experiment for a long time, O_2 impurity concentration in N_2 feed changes a little but not enough to remove NO in the process. The results show that the only one oxygen source in the SCR reaction in the absence of O_2 have effluent to NO removable in the SCR process in absence of O_2. Oxygen is the oxygen source from catalyst itself. The results demonstrate that oxygen from metal oxide species on catalyst might participate in removing NO from the SCR process in the absence of O_2. The lattice oxygen of V_2O_5/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 can participate to remove NO in the SCR process. However, for WO_3/TiO_2 catalyst, the result shows that lattice of oxygen on the catalyst does not participate to remove NO in the SCR process. It might be because V_2O_5/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalyst are easier reduced than WO_3/TiO_2 in the low temperature.

N_2O formation results from the SCR reaction in the absence of O_2 over MoO_3/TiO_2, WO_3/TiO_2, and V_2O_5-MoO_3/TiO_2TiO_2 catalysts demonstrate that oxygen lattice on catalysts have participate to N_2O formation in the SCR process. However, oxygen lattice on V_2O_5 does not produce N_2O from the SCR process.

CHAPTER V
CONCLUSIONS

This chapter shows the conclusions obtained from the experimental results reported and discussed in chapter IV follow :

5.1 Conclusion

1. Stability test results show that V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts are stable under the reaction temperature during the SCR of NO by NH_3 in this experiment.

2. N_2O is formed from the SCR process over V_2O_5/ TiO_2, MoO_3/ TiO_2, and V_2O_5-MoO_3/ TiO_2 catalysts. However, WO_3/ TiO_2 and V_2O_5-WO_3/ TiO_2 catalysts do not produce N_2O formed from the SCR process

3. SO_2 in the influent gas affects the NO conversion and N_2O formation in the SCR process. SO_2 in the influent gas increases NH_3 adsorption on the catalyst surface because SO_2 in the SCR process increases the number of Brønsted acid site on the catalyst surface and decreases the amount of Lewis acid site on the catalyst surface.

4. Lattice oxygen (O^{-2}) of V_2O_5/ TiO_2, MoO_3/ TiO_2 and V_2O_5-MoO_3/ TiO_2 can the SCR process at the high reaction temperature. O^{-2} on MoO_3/ TiO_2 and V_2O_5-MoO_3/ TiO_2 catalysts is participate in increasing N_2O formed from the SCR process. N_2O is formed from the reaction between NH_3 and O_2 rather than NO

5.2 Recommendation for future work

1. Study NO removal and N_2O formation from NH_3 oxidation reaction in the absence of O_2 over V_2O_5/ TiO_2, WO_3/ TiO_2, MoO_3/ TiO_2, V_2O_5-WO_3/ TiO_2 and V_2O_5-MoO_3/ TiO_2 catalysts.

2. Study effect of SO_2 on NH_3 oxidation reaction over V_2O_5/ TiO_2, WO_3/ TiO_2, MoO_3/ TiO_2, V_2O_5-WO_3/ TiO_2 and V_2O_5-MoO_3/ TiO_2 catalysts.

3. Study effect of H_2O on the SCR and NH_3 oxidation reaction in the absence of O_2 over V_2O_5/ TiO_2, WO_3/ TiO_2, MoO_3/ TiO_2, V_2O_5-WO_3/ TiO_2 and V_2O_5-MoO_3/ TiO_2 catalysts.

REFERENCES

1. Ayari, F., et al., *Selective catalytic reduction of NO with* NH_3 *over Cr-ZSM-5 catalysts: General characterization and catalysts screening.* Applied Catalysis B: Environmental, 2013. **134-135**: p. 367-380.

2. Pereda-Ayo, B., et al., *Influence of the washcoat characteristics on* N_{H3}*-SCR behavior of Cu-zeolite monoliths.* Catalysis Today, 2013. **216**: p. 82-89.

3. Metkar, P.S., M.P. Harold, and V. Balakotaiah, *Experimental and kinetic modeling study of* NH_3*-SCR of NOx on Fe-ZSM-5, Cu-chabazite and combined Fe- and Cu-zeolite monolithic catalysts.* Chemical Engineering Science, 2013. **87**: p. 51-66.

4. Ma, Z., et al., *A novel Nb–Ce-WOx–*TiO_2 *catalyst with high* NH_3*-SCR activity and stability.* Catalysis Communications, 2012. **27**(10 July 2012): p. 97–100

5. Metkar, P.S., et al., *Selective catalytic reduction of NO with* NH_3 *on iron zeolite monolithic catalysts: Steady-state and transient kinetics.* Applied Catalysis B: Environmental, 2011. **104**(1-2): p. 110-126.

6. Chen, L., J. Li, and M. Ge, *The poisoning effect of alkali metals doping over nano* V_2O_5*–*WO_3*/*TiO_2 *catalysts on selective catalytic reduction of NOx by* NH_3*.* Chemical Engineering Journal, 2011. **170**(2-3): p. 531-537.

7. Kwak, J.H., et al., *Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NOx with* NH_3*.* Journal of Catalysis, 2010. **275**(2): p. 187-190.

8. Colombo, M., I. Nova, and E. Tronconi, *A comparative study of the* NH_3*-SCR reactions over a Cu-zeolite and a Fe-zeolite catalyst.* Catalysis Today, 2010. **151**(3-4): p. 223-230.

9. Tang, X., et al., *Origination of* N_2O *from NO reduction by* NH_3 *over* β-MnO_2 *and* α-Mn_2O_3*.* Applied Catalysis B: Environmental, 2010. **99**(1-2): p. 156-162.

10. Si, Z., et al., *Structure, acidity and activity of CuOx-WOx–*ZrO_2 *catalyst for selective catalytic reduction of NO by* NH_3*.* Journal of Catalysis 2010. **271**(6 March 2010): p. 43-51.

11. Pietrogiacomi, D., et al., *The effect of sulphation on the catalytic activity of CoOx/*ZrO_2 *for NO reduction with* NH_3 *in the presence of* O_2*.* Applied Catalysis B: Environmental, 2009. **89**(1-2): p. 33-40.

12. Sjövall, H., R.J. Blint, and L. Olsson, *Detailed kinetic modeling of* NH_3 *SCR over Cu-ZSM-5.* Applied Catalysis B: Environmental, 2009. **92**(1-2): p. 138-153.

13. Casapu, M., O. Kröcher, and M. Elsener, *Screening of doped MnOx–*CeO_2 *catalysts for low-temperature NO-SCR.* Applied Catalysis B: Environmental, 2009. **88**(3-4): p. 413-419.

14. Grzybek, T., et al., *Nitrogen promoted active carbons as DeNOx catalysts 1. The influence of modification parameters on the structure and catalytic properties.* Catalysis Today 2008. **137**(31 December 2007): p. 228–234.

15. Grzybek, T., et al., *Nitrogen-promoted active carbons as catalytic supports.* Catalysis Today, 2008. **137**(2-4): p. 235-241.

16. Kröcher, O. and M. Elsener, *Chemical deactivation of* V_2O_5/WO_3–TiO_2 *SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution.* Applied Catalysis B: Environmental, 2008. **77**(3-4): p. 215-227.

17. Tounsi, H., et al., *Copper loaded hydroxyapatite catalyst for selective catalytic reduction of nitric oxide with ammonia.* Applied Catalysis B: Environmental, 2011. **107**(1-2): p. 158-163.

18. Luo, J.-Y., et al., *Spatially resolving SCR reactions over a Fe/zeolite catalyst.* Applied Catalysis B: Environmental, 2011. **102**(1-2): p. 110-119.

19. Lee, K.J., et al., *Ceria added Sb-V_2O_5/TiO_2 catalysts for low temperature NH_3 SCR: Physico-chemical properties and catalytic activity.* Applied Catalysis B: Environmental, 2013. **142-143**: p. 705-717.

20. Zheng, Y., A.D. Jensen, and J.E. Johnsson, *Deactivation of V_2O_5-WO_3-TiO_2 SCR catalyst at a biomass-fired combined heat and power plant.* Applied Catalysis B: Environmental, 2005. **60**(3-4): p. 253-264.

21. W, K., *Formation of N_2O and SO_3 on mixed metal oxide V-W-Mo/TiO_2 catlyst during the selective catalytic reduction of NO by NH_3* Master's Thesis, Department of Chemical Engineer, Faculty of Chemical Engineer, Chulalongkorn university, 2012(2012).

22. Matralis, H., et al., *Selective catalytic reduction of nitric oxide with ammonia using MoO_3-TiO_2 Catalyst structure and activity.* Applied Catalysis B: Environmental, 1995. **5**(1995): p. 271-281.

23. Amiridisa, D., R. Duevelb, and I. Wachs, *The effect of metal oxide additives on the activity of V_2O_5-TiO_2 catalysts for the selective catalytic reduction of nitric oxide by ammonia.* Applied Catalysis B: Environmental, 1999. **20**(29 September 1998): p. 111-122.

24. Casagrande, L., et al., *SCR of NO by NH_3 over TiO_2-supported V_2O_5–MoO_3 catalysts reactivity and redox behavior.* Applied Catalysis B: Environmental 1999. **22**(20 March 1999): p. 63–77.

25. Kamata, H., K. Takahashi, and C.U.I. Odenbrand, *Kinetics of the Selective Reduction of NO with NH_3 over a V_2O_5(WO_3)-TiO_2 Commercial SCR Catalyst.* Journal of Catalysis, 1999. **185**(March 4, 1999): p. 106-113.

26. Kamata, H., K. Takahashi, and C.U.I. Odenbrand, *The role of K_2O in the selective reduction of NO with NH_3 over a $V_2O_5(WO_3)$-TiO_2 commercial selective catalytic reduction catalyst.* Journal of Molecular Catalysis A: Chemical 1999. **139**(19 May 1998): p. 189–198

27. Long, R.Q. and R.T. Yang, *Selective catalytic reduction of NO with ammonia over V_2O_5 doped TiO_2 pillared clay catalysts.* Applied Catalysis B: Environmental 2000. **24**(30 June 1999): p. 13–21.

28. Nova, I., et al., *Dynamics of SCR reaction over a TiO_2-supported vanadia–tungsta commercial catalyst.* Catalysis Today 2000. **60**(2000): p. 73-82.

29. Fountzoula, C., et al., *Molybdenum-titanium oxide catalysts the influence of the preparation conditions on their activity for the selective catalytic reduction of NO by NH_3.* Applied Catalysis B: Environmental 2002. **35**(9 September 2001): p. 295–304.

30. Due-Hansen, J., et al., *Vanadiabased SCR catalysts supported on tungstated and sulfated zirconia Influence of doping with potassium.* Journal of Catalysis, 2007. **250**(5 September 2007): p. 459 – 473

31. Phil, H.H., et al., *SO2 resistant antimony promoted V_2O_5/TiO_2 catalyst for NH_3-SCR of NOx at low temperatures.* Applied Catalysis B: Environmental, 2008. **78**(3-4): p. 301-308.

32. Khalfallah Boudali, L., A. Ghorbel, and P. Grange, *Characterization and reactivity of WO_3–V_2O_5 supported on sulfated titanium pillared clay catalysts for the SCR-NO reaction.* Comptes Rendus Chimie, 2009. **12**(6-7): p. 779-786.

33. Tang, F., et al., *The poisoning effect of Na^+ and Ca^{2+} ions doped on the V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO by NH_3.* Applied Catalysis B: Environmental, 2010. **94**(1-2): p. 71-76.

34. Klimczak, M., et al., *High-throughput study of the effects of inorganic additives and poisons on NH_3-SCR catalysts—Part I: V_2O_5–WO_3/TiO_2 catalysts.* Applied Catalysis B: Environmental, 2010. **95**(1-2): p. 39-47.

35. Shi, A., et al., *The effect of zirconia additive on the activity and structure stability of V_2O_5/WO_3-TiO_2 ammonia SCR catalysts.* Applied Catalysis B: Environmental, 2011. **106**(3-4): p. 359-369.

36. Li, Q., et al., *Promotional effects of carbon nanotubes on V_2O_5/TiO_2 for NOX removal.* J Hazard Mater, 2011. **192**(2): p. 915-21.

37. Zhang, H., et al., *Study of synthesis and catalytic property of WO_3/TiO_2 catalysts for NO reduction at high temperatures.* Journal of Molecular Catalysis A: Chemical, 2011. **350**(1-2): p. 35-39.

38. Chen, X., et al., *Selective catalytic reduction of NO over carbon nanotubes supported CeO_2.* Catalysis Communications, 2011. **14**(1): p. 1-5.

39. Kompio, P., et al., *A new view on the relations between tungsten and vanadium in V_2O_5 single bond WO_3-TiO_2 catalysts for the selective reduction of NO with NH_3.* Journal of Catalysis, 2012. **286**(10 December 2011): p. 237–247.

40. Forzatti, P., et al., *Effect of operating variables on the enhanced SCR reaction over a commercial V_2O_5–WO_3/TiO_2 catalyst for stationary applications.* Catalysis Today, 2012. **184**(1): p. 153-159.

41. Casanova, M., et al., *Improved high temperature stability of NH_3-SCR catalysts based on rare earth vanadates supported on $TiO_2WO_3SiO_2$.* Catalysis Today, 2012. **184**(1): p. 227-236.

42. Wang, C., et al., *Dispersion of tungsten oxide on SCR performance of $V_2O_5WO_3/TiO_2$: Acidity, surface species and catalytic activity.* Chemical Engineering Journal, 2013. **225**: p. 520-527.

43. Cha, W., et al., *Enhanced low-temperature NH_3-SCR activity of a V_2O_5/TiO_2 composite prepared via chemical vapor condensation and impregnation method.* Materials Research Bulletin, 2013. **48**(10): p. 4415-4418.

44. Lei, Z., et al., *Influence of H_2O on the low-temperature NH_3-SCR of NO over V_2O_5/AC catalyst: An experimental and modeling study.* Chemical Engineering Journal, 2013. **215-216**: p. 651-657.

45. Pan, Y., et al., *Promotional effect of Si-doped V_2O_5/TiO_2 for selective catalytic reduction of NO x by NH_3.* Journal of Environmental Sciences, 2013. **25**(8): p. 1703-1711.

46. Yu, W., et al., *Influences of impregnation procedure on the SCR activity and alkali resistance of V_2O_5–WO_3/TiO_2 catalyst.* Applied Surface Science, 2013. **283**: p. 209-214.

47. Zhang, S., Q. Zhong, and Y. Wang, *Effect of rutile phase on V_2O_5 supported over TiO_2 mixed phase for the selective catalytic reduction of NO with NH_3.* Applied Surface Science, 2014. **314**: p. 112-118.

48. Liu, Z., et al., *Selective catalytic reduction of NOx by NH3 over MoO3-promoted CeO_2/TiO_2 catalyst.* Catalysis Communications, 2014. **46**: p. 90-93.

49. Yang, J., et al., *Low-cost V–W–Ti SCR catalyst from titanium-bearing blast furnace slag.* Journal of Environmental Chemical Engineering, 2014. **2**(27 March 2014): p. 1007–1010.

50. Zhang, Q.-m., et al., *Effect of metal oxide partial substitution of* V_2O_5 *in* V_2O_5*–*WO_3*/*TiO_2 *on selective catalytic reduction of NO with* NH_3*.* Journal of Industrial and Engineering Chemistry, 2015. **24**: p. 79-86.

51. Zhao, B., et al., *Effect of molybdenum on mercury oxidized by* V_2O_5*–*MoO_3*/*TiO_2 *catalysts.* Chemical Engineering Journal, 2014. **253**: p. 508-517.

APPENDIX

APPENDIX A.

NO CONVERSION AND N_2O FORMATION RESULTS

Appendix A includes NO conversion and N_2O conversion raw results during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts

A.1 NO conversion

NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts are shown in Table A.1-A.5 below :

Table A.1 NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5/TiO_2 catalyst

Temperature (°C)	%NO conversion		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	10.81	11.55	0.00
200	8.70	29.71	0.00
250	28.20	100.00	0.00
300	54.10	100.00	0.00
350	44.00	40.81	0.00
400	29.80	10.98	11.79
450	31.20	0.00	44.84

Table A.2 NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over WO_3/TiO_2 catalyst

Temperature (°C)	%NO conversion		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	5.47	0.00	0.00
300	18.56	16.76	0.00
350	33.65	32.27	0.00
400	37.40	34.80	0.00
450	26.89	14.56	0.00

Table A.3 NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over MoO_3/TiO_2 catalyst

Temperature (°C)	%NO conversion		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	5.34	7.00	0.00
300	19.64	11.80	0.00
350	41.23	23.30	17.57
400	39.73	40.31	24.85
450	32.35	16.29	48.09

Table A.4 NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5-WO_3/TiO_2 catalyst

Temperature (°C)	%NO conversion		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	10.34	24.16	0.00
200	25.51	39.76	0.00
250	33.82	100.00	0.00
300	100.00	100.00	0.00
350	100.00	54.16	0.00
400	26.15	24.06	32.74
450	0.00	0.00	67.08

Table A.5 NO conversion during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5-MoO_3/TiO_2 catalyst

Temperature (°C)	%NO conversion		
	SCR	The SCR in the absence of SO_2	The SCR in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	9.24	17.81	0.00
250	32.43	37.17	10.58
300	50.13	49.70	30.20
350	17.30	19.41	57.00
400	0.00	11.02	53.90
450	0.00	0.00	46.46

A.2 N_2O formation

N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts are shown in Table A.6-A.7 below :

Table A.6 N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5/TiO_2 catalyst

Temperature (°C)	N_2O formation (ppm)		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	0.00	0.00	0.00
300	0.00	0.00	0.00
350	0.00	3.99	0.00
400	5.18	5.24	0.00
450	9.72	4.60	0.00

Table A.7 N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over WO_3/TiO_2 catalyst

Temperature (°C)	N_2O formation (ppm)		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	0.00	0.00	0.00
300	0.00	17.48	5.29
350	0.00	18.46	0.00
400	0.00	15.73	0.00
450	0.00	6.84	0.00

Table A.8 N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over MoO_3/TiO_2 catalyst

Temperature (°C)	N_2O formation (ppm)		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	5.76	4.23	21.35
300	11.62	6.05	22.12
350	32.18	6.35	38.92
400	43.33	11.95	46.25
450	34.91	10.54	20.51

Table A.9 N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5-WO_3/TiO_2 catalyst

Temperature (°C)	N_2O formation (ppm)		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	0.00	0.00	0.00
300	0.00	0.00	0.00
350	0.00	0.00	0.00
400	0.00	0.00	0.00
450	0.00	0.00	0.00

Table A.10 N_2O formation during the SCR process, the SCR process in the absence of SO_2 and the SCR process in the absence of O_2 over V_2O_5-MoO_3/TiO_2 catalyst

Temperature (°C)	N_2O formation (ppm)		
	SCR	The SCR process in the absence of SO_2	The SCR process in the absence of O_2
120	0.00	0.00	0.00
150	0.00	0.00	0.00
200	0.00	0.00	0.00
250	0.00	0.00	11.70
300	0.00	0.00	35.60
350	23.77	21.60	43.61
400	28.23	25.41	61.46
450	27.79	12.40	57.01

APPENDIX B.

NH_3-TPD RESULTS

Appendix B shows graph between TCD signal (a.u.) and time (min) in the NH_3-TPD experimental for TiO_2, V_2O_5/TiO_2, WO_3/TiO_2, MoO_3/TiO_2, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts. The results are shown in Figure B.1-B.6 below :

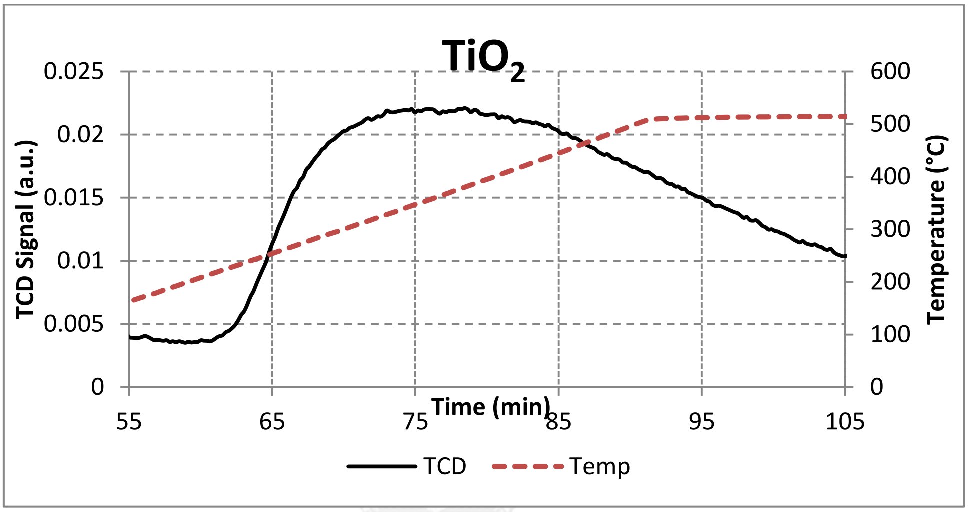

Figure B.1 NH_3-TPD for TiO_2 catalyst.

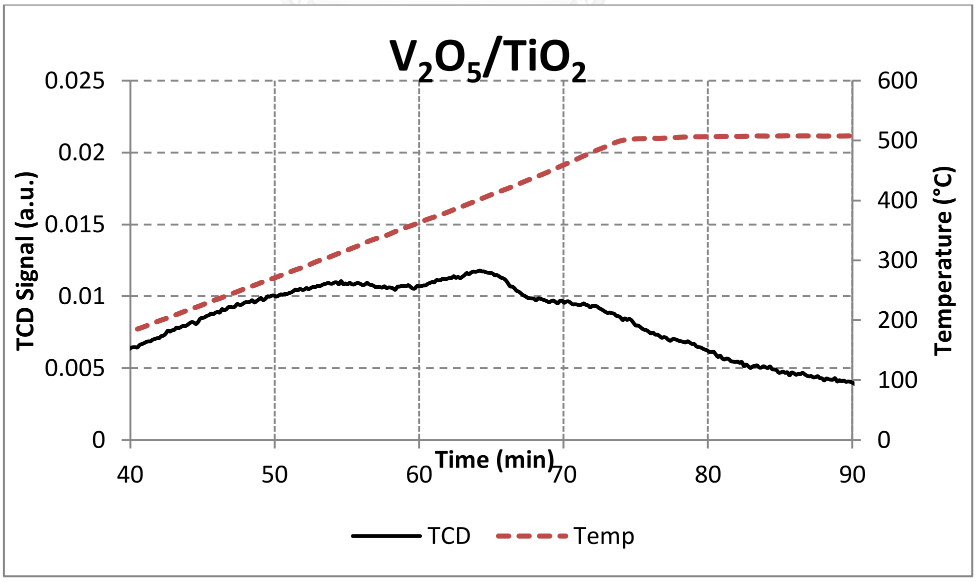

Figure B.2 NH_3-TPD for V_2O_5/TiO_2 catalyst.

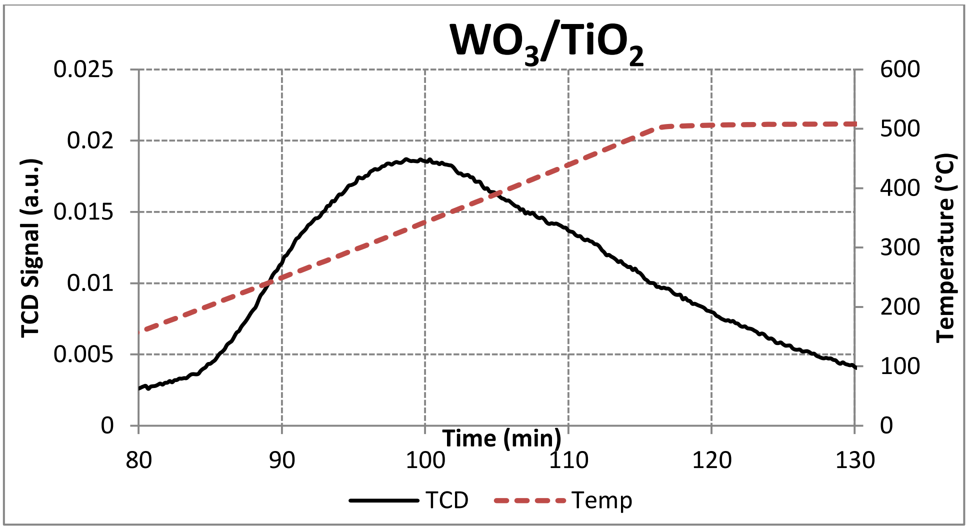

Figure B.3 NH_3-TPD for WO_3/TiO_2 catalyst.

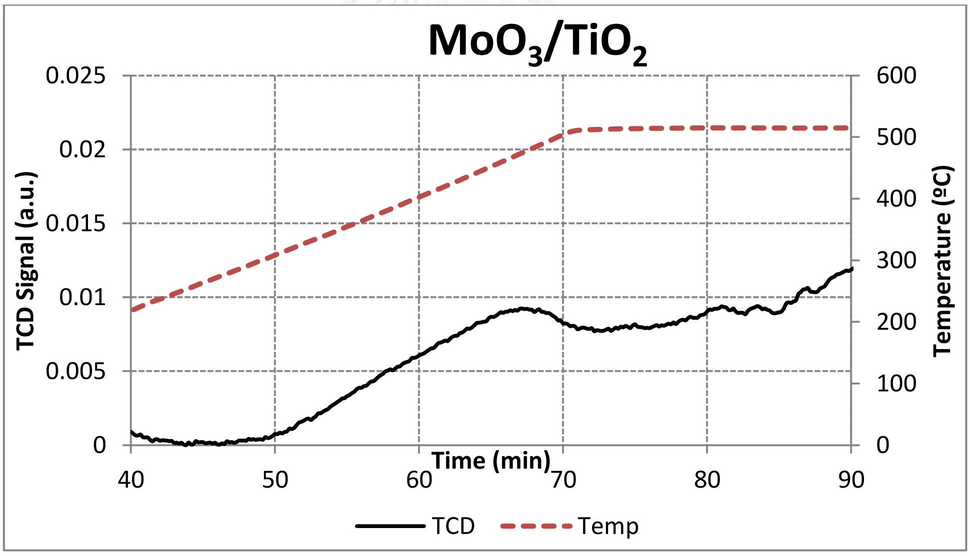

Figure B.4 NH_3-TPD for MoO_3/TiO_2 catalyst.

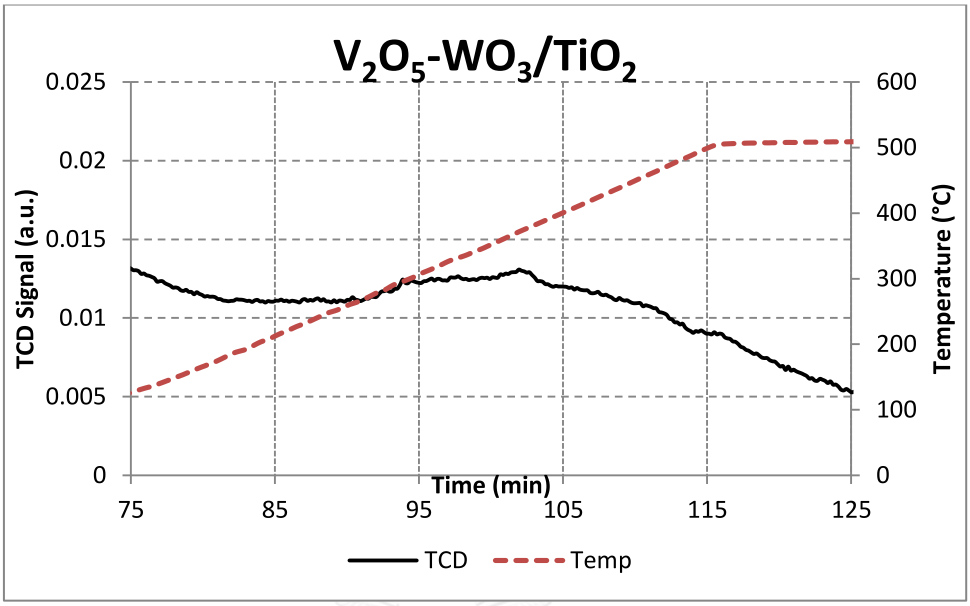

Figure B.5 NH_3-TPD for V_2O_5-WO_3/TiO_2 catalyst.

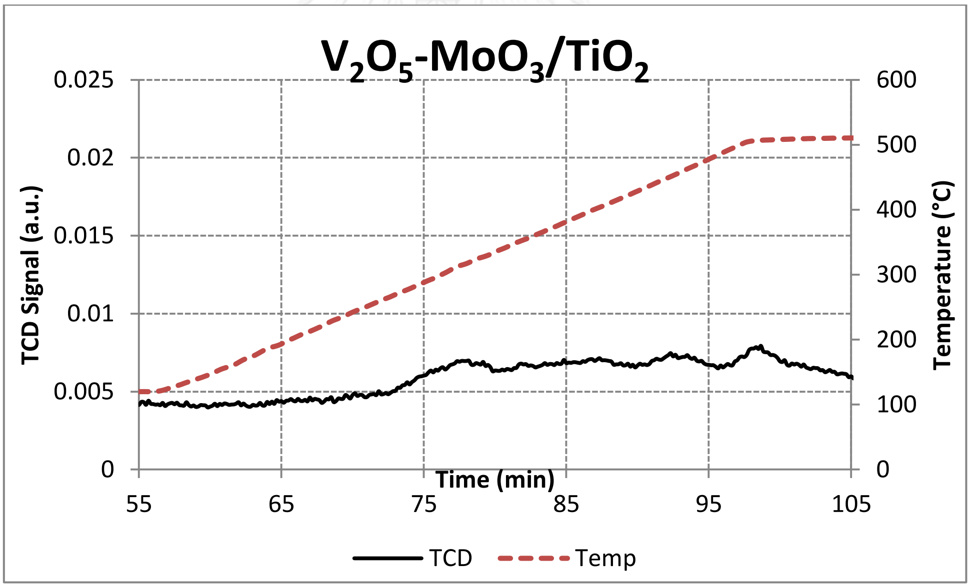

Figure B.6 NH_3-TPD for V_2O_5-MoO_3/TiO_2 catalyst.

APPENDIX C.

CACULATION FOR CATALYST PREPARATION

Appendix C shows example calculation for catalyst preparation. Using V_2O_5/TiO_2 and V_2O_5-WO_3/TiO_2 catalysts are example calculation.

C.1 V_2O_5/TiO_2 preparation.

Reagent :

- Titanium powder (P-25)
- Ammonium metavanadate (NH_4VO_3) 99.999%
- Oxalic acid hydrate

3wt% V_2O_5/TiO_2 based on 2 g of catalyst used, the composition of the catalyst will be as follows :

V_2O_5 = 0.03x2 = 0.06 g

TiO_2 = 2-0.06 = 1.94 g

V_2O_5 0.06 g was prepared from NH_4VO_3 (MW. = 117 g/mole) as shows below :

Mol of V_2O_5 = 0.06/181.88 mol

= $3.30\text{x}10^{-4}$ mol

Mol of V = $3.30\text{x}10^{-4}$ x 2 mol

= $6.60\text{x}10^{-4}$ mol

Weigh of V (50.94 g/mol) = $6.60\text{x}10^{-4}$ x 50.94 g

= 0.03 g

NH_4VO_3 required = (0.033 x 117)/51 g

= 0.08 g

Oxalic acid required (MW. = 126.07 g/mole) is shown below :

Mol Oxalic acid required = Mol V_2O_5

= $3.30\text{x}10^{-4}$ mol

Oxalic acid required = $3.30\text{x}10^{-4}\text{x}126.07$ g

= 0.042 g

C.2 V_2O_5–WO_3/TiO_2 preparation.

Reagent :

- Titanium powder (P-25)
- Ammonium metavanadate (NH_4VO_3) 99.999%
- Ammonium metatungsteae hydrate ($(NH_4)_6H_2W_{12}O_{40}xH_2O$) 99.99%
- Oxalic acid hydrate

3% V_2O_5 – 7.5wt% WO_3/TiO_2 based on 2 g of catalyst used, the composition of the catalyst will be as follows :

V_2O_5 = 0.03x2 = 0.06 g

WO_3 = 0.07x2 = 0.14 g

TiO_2 = 2-0.06-0.14 = 1.80 g

V_2O_5 0.06 g was prepared from NH_4VO_3 (MW. = 117 g/mole) as shows below :

Mol of V_2O_5 = 0.06/181.88 mol

= $3.30\text{x}10^{-4}$ mol

Mol of V = $3.30\text{x}10^{-4}$ x 2 mol

= $6.60\text{x}10^{-4}$ mol

Weigh of V (50.94 g/mol) = $6.60\text{x}10^{-4}$ x 50.94 g

= 0.033 g

NH_4VO_3 required = (0.033 x 117)/51 g

= 0.07 g

WO_3 0.15 g was prepared from $(NH_4)_6H_2W_{12}O_{40}xH_2O$ (MW. = 2956.3 g/mole) as shows below :

Mol WO_3 = 0.15/231.84 mol

= $6.47x10^{-4}$ mol

Mol W = mol WO_3

= $6.47x10^{-4}$ mol

$(NH_4)_6H_2W_{12}O_{40}xH_2O$ required = mol W / 12 mol

= $6.47x10^{-4}/12$ mol

= $5.39x10^{-5}$ mol

= $5.39x10^{-5}x2956.3$ g

= 0.16 g

Oxalic acid required (MW. = 126.07 g/mole) is shown below :

<u>WO_3</u> Mol Oxalic acid required = Mol WO_3

= $6.47x10^{-4}$ mol

Oxalic acid required = $6.47x10^{-4}x126.07$ g

= 0.08 g

<u>V_2O_5</u> Mol Oxalic acid required = Mol V_2O_5

= $3.30x10^{-4}$ mol

Oxalic acid required = $3.30x10^{-4}x126.07$ g

= 0.04 g

Total Mol Oxalic acid required = 0.08+0.04 g

=0.12 g

VITA

Miss Archareeyaporn Ruengthawornkul was born on July 15, 1990 in Ubonratchathanee, Thailand. She finished high school from Benchama maharat school, Ubonratchathanee, Thailand. She graduated the bachelor’s degree from Department of Chemical Engineering, Faculty of Engineer, Mahidol University, Bangkok, Thailand, April 2013. She continued her master’s degree at Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University in 2013.