

ผลของการโดปซิลเวอร์ออกไซด์และคอปเปอร์ออกไซด์บนตัวเร่งปฏิกิริยา  $V_2O_5-WO_3-TiO_2$  ใน  
ปฏิกิริยารีดักชันแบบเลือกเกิดที่ใช้ตัวเร่งปฏิกิริยาของก๊าซไนโตรเจนออกไซด์  
โดยแอมโมเนียที่อุณหภูมิต่ำ



บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)  
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)  
are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต  
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี  
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2557  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECT OF SILVER AND COPPER OXIDES DOPING ON  $V_2O_5$ - $WO_3$ - $TiO_2$   
CATALYST FOR LOW-TEMPERATURE SELECTIVE CATALYTIC REDUCTION  
OF NITROGEN OXIDE BY AMMONIA

Mr. Natthakorn Jirathanasin



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  
Copyright of Chulalongkorn University



ณัฐกร จิรนาสิน : ผลของการโดปซิลเวอร์ออกไซด์และคอปเปอร์ออกไซด์บนตัวเร่งปฏิกิริยา  $V_2O_5-WO_3-TiO_2$  ในปฏิกิริยารีดักชันแบบเลือกเกิดที่ใช้ตัวเร่งปฏิกิริยาของก๊าซไนโตรเจนออกไซด์โดยแอมโมเนียที่อุณหภูมิต่ำ (EFFECT OF SILVER AND COPPER OXIDES DOPING ON  $V_2O_5-WO_3-TiO_2$  CATALYST FOR LOW-TEMPERATURE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร.อัครวัต ศิริสุข, 69 หน้า.

วิทยานิพนธ์ชิ้นนี้จัดทำเพื่อศึกษาผลของการเติมซิลเวอร์ออกไซด์และคอปเปอร์ออกไซด์บนตัวเร่งปฏิกิริยา  $V_2O_5-WO_3-TiO_2$  ในปฏิกิริยารีดักชันแบบเลือกเกิดที่ใช้ตัวเร่งปฏิกิริยาของก๊าซไนโตรเจนออกไซด์โดยแอมโมเนียที่อุณหภูมิต่ำ ด้วยการโดปซิลเวอร์ออกไซด์และคอปเปอร์ออกไซด์ในตัวเร่งปฏิกิริยาอยู่ในช่วงร้อยละ 2 ถึง 6 โดยน้ำหนัก ในขณะที่ปริมาณของวอานาเดียมออกไซด์และทังสเตนออกไซด์ให้คงที่ร้อยละ 3 และ 7 โดยน้ำหนัก ตามลำดับ โดยใช้การเตรียมตัวรองรับ  $TiO_2$  ด้วยวิธีโซลเจลแล้วทำการเติมโลหะออกไซด์ชนิดต่างๆด้วยวิธีการเคลือบฝังแบบเปียก ตัวเร่งปฏิกิริยาทั้งหมดในงานวิจัยนี้ถูกนำไปวิเคราะห์เพื่อตรวจสอบคุณสมบัติทางกายภาพและเคมีด้วยวิธีการดูดซับด้วยไนโตรเจน ICP-OES XRD และ  $NH_3$ -TPD การตรวจสอบความสามารถของตัวเร่งปฏิกิริยาสำหรับปฏิกิริยารีดักชันของไนโตรเจนออกไซด์แบบเลือกเกิดด้วยแอมโมเนียถูกวัดโดยเครื่องแก๊สโครมาโตกราฟี ในช่วงอุณหภูมิตั้งแต่ 120-400 องศาเซลเซียส จากการศึกษาพบว่าตัวเร่งปฏิกิริยาทั้งหมดที่มีการเติมซิลเวอร์ออกไซด์ลงไปในตัวเร่งปฏิกิริยา  $V_2O_5-WO_3/TiO_2$  ส่งผลให้ประสิทธิภาพการทำงานของตัวเร่งปฏิกิริยาลดน้อยลง ในทางตรงกันข้ามการเติมคอปเปอร์ออกไซด์ลงไปในตัวเร่งปฏิกิริยา  $V_2O_5-WO_3/TiO_2$  ส่งผลให้การทำงานของตัวเร่งปฏิกิริยาดีขึ้น โดยเฉพาะอย่างยิ่งกับตัวเร่งปฏิกิริยา  $V_2O_5-WO_3/TiO_2$  ที่มีองค์ประกอบของคอปเปอร์ออกไซด์ที่ร้อยละ 2 และ 6 โดยน้ำหนัก ผลที่ได้คือเมื่อมีการเติมคอปเปอร์ออกไซด์ที่ร้อยละ 2 โดยน้ำหนัก ส่งผลให้การทำงานของตัวเร่งปฏิกิริยาเพิ่มมากขึ้นในช่วงอุณหภูมิสูง และการเติมคอปเปอร์ออกไซด์ที่ร้อยละ 6 โดยน้ำหนัก ส่งผลให้การทำงานของตัวเร่งปฏิกิริยาเพิ่มมากขึ้นในช่วงอุณหภูมิสูง

ภาควิชา วิศวกรรมเคมี

ลายมือชื่อนิสิต .....

สาขาวิชา วิศวกรรมเคมี

ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

ปีการศึกษา 2557

# # 5570184121 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: SELECTIVE CATALYTIC REDUCTION (SCR) / SILVER OXIDE / COPPER OXIDE / V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> CATALYST / NH<sub>3</sub>-SCR / DENOX

NATTHAKORN JIRATHANASIN: EFFECT OF SILVER AND COPPER OXIDES DOPING ON V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> CATALYST FOR LOW-TEMPERATURE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA. ADVISOR: AKAWAT SIRISUK, Ph.D., 69 pp.

This research investigated effect of silver and copper oxides doping on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts, prepared by impregnation method, for selective catalytic reduction of NO<sub>x</sub> by ammonia at low temperature. The amounts of Ag<sub>2</sub>O and Cu<sub>2</sub>O were varied in ranged of 2%wt to 6%wt, while the amounts of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> in the catalysts were fixed at 3%wt. and 7%wt., respectively. TiO<sub>2</sub> support was prepared by sol-gel method. All studied catalysts were characterized by diverse techniques such as N<sub>2</sub>-physisorption, ICP-OES, XRD and NH<sub>3</sub>-TPD. The catalytic activity testing of NH<sub>3</sub>-SCR was measured by gas chromatography. Reaction temperature was varied from 120 to 400°C. The addition of silver oxide influenced decreasing performance of the catalyst. In contrast, the addition of copper oxide enhanced the catalytic activity, especially, the copper oxide containing in 2 and 6 %wt. catalyst were observed. From the results, explicit trends in two different temperature regions was occurred in term of copper oxide loading. With 2%wt.Cu<sub>2</sub>O loading, catalytic activity increased at high temperature, while catalytic activity of 6%wt.Cu<sub>2</sub>O loading enhanced at low temperature.

Department: Chemical Engineering

Student's Signature .....

Field of Study: Chemical Engineering

Advisor's Signature .....

Academic Year: 2014

## ACKNOWLEDGEMENTS

The author would like to appreciate for precious suggestions, valuable guidance and the vision thought out this research to his advisor, Dr. Akawat Sirisuk, and special thanks for all supporters who gave helpful and useful to this research such as Professor Dr. Piyasan Prasertdam, as the chairman, Professor Dr. Suthichai Assabumrungrat and Dr. Kanokwan Ngaosuwan as committees.

Sincerely appreciate the useful help from Associate Professor Dr. Tharathon Mongkonsri and members of the Center of Excellence on Catalysis and Catalytic Reaction Engineering of Chulalongkorn University, who always give the motivation and encouragement along this thesis study.

The financial for this research was supported by the PTT Public Company Limited.

Eventually, the author would like to dedicate the accomplishment of this work to his parents who have always been the source of his support and encouragement.

## CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT .....	v
ACKNOWLEDGEMENTS .....	vi
CONTENTS .....	vii
LIST OF TABLES .....	ix
LIST OF FIGURES .....	x
CHAPTER 1.....	1
INTRODUCTION .....	1
1.1 General introduction.....	1
1.2 Research objectives .....	4
1.3 Research scopes .....	4
1.4 Research methodology.....	5
CHAPTER 2.....	6
THEORY AND LITERATURE REVIEWS .....	6
CHAPTER 3.....	20
EXPERIMENTAL.....	20
3.1 Catalyst preparation .....	20
3.2 Characterization of catalyst.....	22
3.3 Catalytic activity testing system.....	24
CHAPTER 4.....	27
RESULTS AND DISCUSSIONS.....	27
4.1 Catalytic characterization .....	27

	Page
4.2 Selective catalytic reduction of nitrogen oxide by ammonia.....	33
CHAPTER 5.....	44
CONCLUSIONS AND RECOMMENDATIONS .....	44
5.1 Conclusions .....	44
5.2 Recommendations .....	45
REFERENCES .....	46
APPENDICES.....	55
APPENDIX A.....	56
APPENDIX B .....	60
APPENDIX C.....	64
APPENDIX D.....	66
APPENDIX E .....	68
VITA.....	69





## LIST OF TABLES

	Page
<b>Table 3.1</b> List of catalysts used in this study. ....	20
<b>Table 4.1</b> The composition of metal oxide contained in $V_2O_5$ - $WO_3$ - $TiO_2$ and $Ag_2O$ -doped $V_2O_5$ - $WO_3$ - $TiO_2$ catalysts.....	28
<b>Table 4.2</b> The composition of metal oxide contained in $V_2O_5$ - $WO_3$ - $TiO_2$ and $Cu_2O$ -doped $V_2O_5$ - $WO_3$ - $TiO_2$ catalysts.....	28
<b>Table 4.3</b> Specific surface area of $TiO_2$ support and studied catalysts.....	31
<b>Table 4.4</b> Total acid sites of studied catalysts.....	32
<b>Table C.1</b> Total area under peak of studied catalysts .....	64
<b>Table D.1</b> Peak area of NO at each temperature for 3V7W4Cu catalyst.....	66
<b>Table E.1</b> Operating condition of Shimadzu GC-2014.....	68

## LIST OF FIGURES

	Page
<b>Figure 3.1</b> Flow diagram of the reactor system for SCR of NO by NH <sub>3</sub> .....	25
<b>Figure 4.1</b> XRD patterns of TiO <sub>2</sub> support and catalysts .....	29
<b>Figure 4.2</b> Catalytic activity of V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> catalyst for NH <sub>3</sub> -SCR reaction .....	34
<b>Figure 4.3</b> NH <sub>3</sub> oxidation of V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> catalyst.....	36
<b>Figure 4.4</b> Comparison of catalytic activity for NH <sub>3</sub> -SCR reaction by different loading of silver over V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> catalyst.....	37
<b>Figure 4.5</b> Comparison of catalytic activity for NH <sub>3</sub> -SCR reaction by different loading of copper over V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> catalyst.....	39
<b>Figure 4.6</b> NH <sub>3</sub> oxidation of 3V7W2Cu catalyst.....	41
<b>Figure 4.7</b> NH <sub>3</sub> oxidation of 3V7W4Cu catalyst.....	42
<b>Figure 4.8</b> NH <sub>3</sub> oxidation of 3V7W6Cu catalyst.....	42
<b>Figure B.1</b> NH <sub>3</sub> -TPD profile of 3V7W catalyst.....	60
<b>Figure B.2</b> NH <sub>3</sub> -TPD profile of 3V7W2Ag catalyst.....	61
<b>Figure B.3</b> NH <sub>3</sub> -TPD profile of 3V7W4Ag catalyst.....	61
<b>Figure B.4</b> NH <sub>3</sub> -TPD profile of 3V7W6Ag catalyst.....	62
<b>Figure B.5</b> NH <sub>3</sub> -TPD profile of 3V7W2Cu catalyst .....	62
<b>Figure B.6</b> NH <sub>3</sub> -TPD profile of 3V7W4Cu catalyst .....	63
<b>Figure B.7</b> NH <sub>3</sub> -TPD profile of 3V7W6Cu catalyst .....	63
<b>Figure C.1</b> Calibration curve of NH <sub>3</sub> .....	65

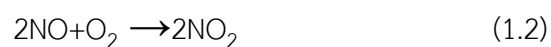
## CHAPTER 1

### INTRODUCTION

#### 1.1 General introduction

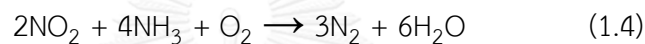
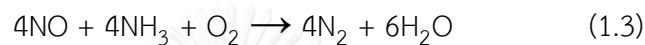
The emission of nitrogen oxides (NO, NO<sub>2</sub> and N<sub>2</sub>O is generally called NO<sub>x</sub>) becomes a primary concern with the air pollutions such as photochemical smog, acid rain, ozone depletion and green-house effects. Regularly, engine exhausts NO<sub>x</sub> being a mixture which consist of 95% NO and 5% NO<sub>2</sub>. There are three types of NO<sub>x</sub> formed from the combustion process, namely, thermal NO<sub>x</sub> formed by the oxidation of nitrogen at high temperature, fuel NO<sub>x</sub> formed from the oxidation of nitrogen in the presence of coal or heavy oils and prompt NO<sub>x</sub> formed by the reaction between atmospheric nitrogen and hydrocarbon fragments [1]. NO<sub>x</sub>, which are released from automobiles and stationary sources, can damage human health, leading to bronchitis, emphysema and pneumonia [2]. Therefore, the decrease in nitrogen oxides (DeNO<sub>x</sub>) is intended to reduce emission of environmentally unacceptable compounds.

The stringent worldwide emission regulations due to the ecological and health hazards motivate to reduce NO<sub>x</sub>. Commonly, NO<sub>x</sub> are thermal NO<sub>x</sub>, which are produced during the combustion process at high temperature based on following steps:

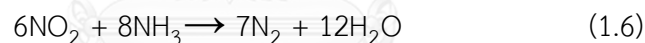
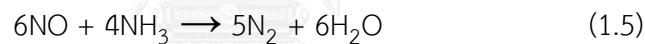


Catalytic technologies are widely applied owing to their low cost and high efficiency. The selective catalytic reduction (SCR) is one of the abatement solutions for  $\text{NO}_x$  in flue gas from stationary sources. Japan has first developed this technology in the 1970s and it has been employed widely by using ammonia as a reducing agent [3].

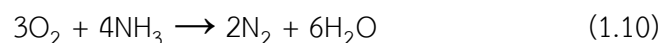
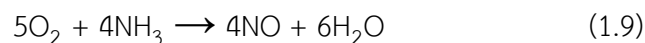
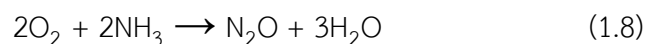
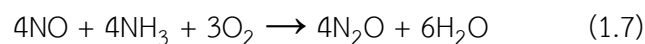
Typically,  $\text{NH}_3$ -SCR is based on the reduction of  $\text{NO}_x$  with  $\text{NH}_3$  and form nitrogen and water as products.



In the absence of oxygen the reaction is converted to the following steps.



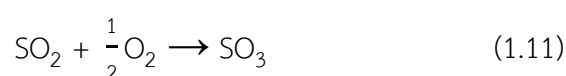
However, the unwanted product ( $\text{N}_2\text{O}$ ) can be formed through these reaction.



An SCR reactor locating at the upstream of the purification units, at which the flue gas is relatively cleaned by passing through the electrostatic precipitator and the desulfurizer, can deactivate catalyst due to poisoning of sulfur and dust deposition

from ash. In order to prevent deactivation of the catalyst, the SCR reactor should be located as the downstream unit [4]. In general, the temperatures of flue gas are about 200°C. Therefore, one needs to develop a catalyst that gives high activity for SCR process at low temperature.

In case of presence of SO<sub>2</sub> in the combustion gases, SO<sub>3</sub> can appear over the catalyst based on the following oxidation reaction.



The undesirable oxidation of SO<sub>2</sub> to SO<sub>3</sub> may result in the deposition and corrosion of SCR downstream unit. In fact, most of low-temperature NH<sub>3</sub>-SCR catalysts are sensitive to sulfur poisoning due to the accumulation of sulfur on the active sites, leading to catalyst deactivation [5].

For industrial applications, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> promoted with WO<sub>3</sub> is the widely-used catalyst for the SCR process. Anatase TiO<sub>2</sub> is generally used as a support due to its excellent sulfur tolerance and V<sub>2</sub>O<sub>5</sub> is the active phase. Although V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst is the most commonly used, there are some disadvantages such as the toxicity of vanadium, the narrow performance window located at 300-400°C and catalyst deactivation occurring because of ash, alkali oxide, SO<sub>2</sub> and salt in the flue gas. To enhance the activity of SCR process, addition of silver and copper to an SCR catalyst are studied. Silver ions and ionic silver, on the surface of Ag/ZSM-5, can be active in the SCR of NO<sub>x</sub> by using propene as the reducing agent [6]. Similarly, CuO species over various supports are found to be active in the reduction of NO by light hydrocarbon, CO and hydrogen [7-10].

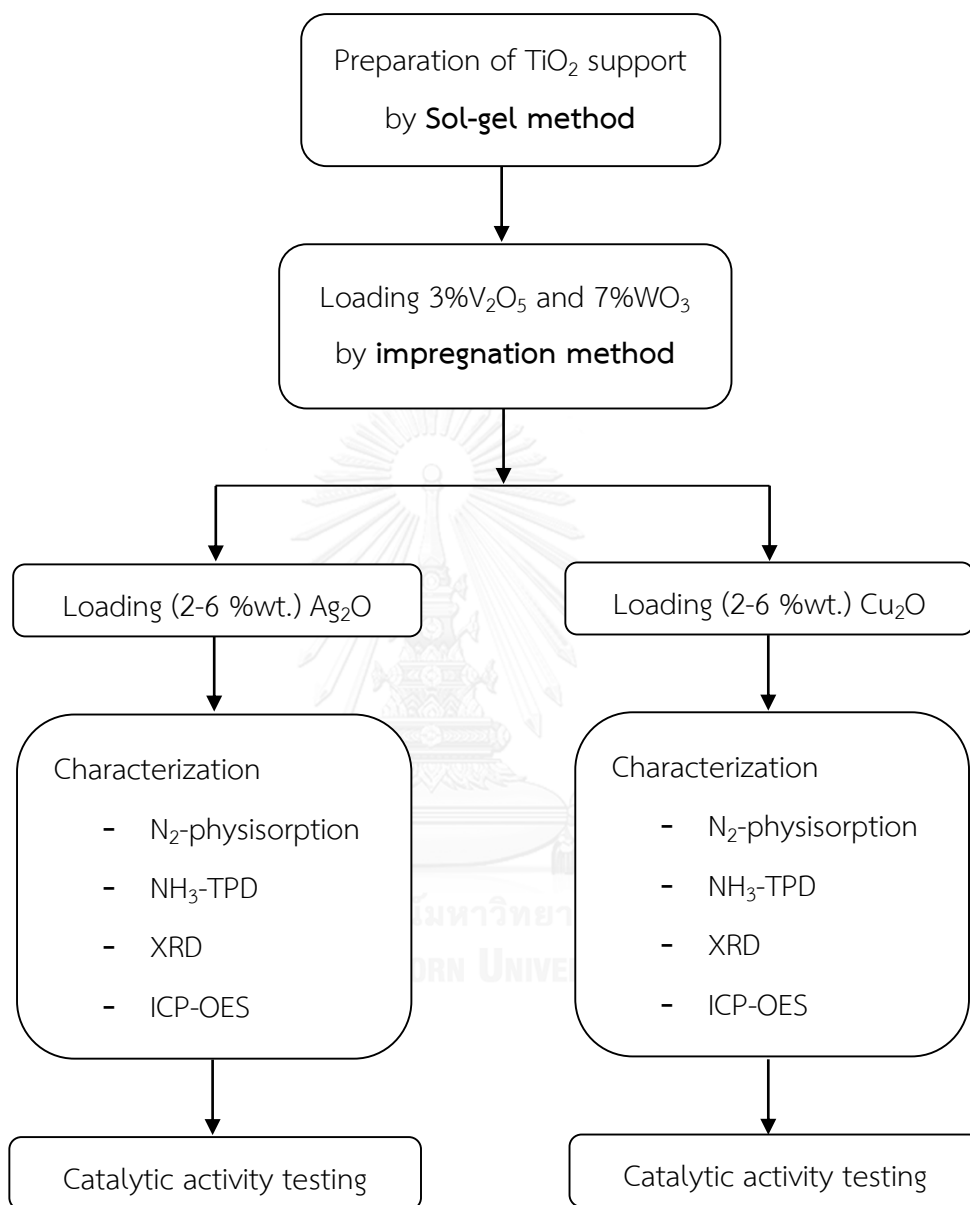
## 1.2 Research objectives

The objective of this research is to investigate the effect of silver and copper oxides doping on  $V_2O_5-WO_3/TiO_2$  catalysts prepared by impregnation method for selective catalytic reduction of  $NO_x$  by ammonia at low temperature.

## 1.3 Research scopes

- Preparation of  $TiO_2$  support is prepared by a sol-gel method.
- $V_2O_5-WO_3/TiO_2$  catalyst is prepared by incipient wetness impregnation method.
- $V_2O_5-WO_3/TiO_2$  catalyst is doped with silver and/or copper in the range of 2-6%wt. (prepared by incipient wetness impregnation).
- $TiO_2$  support and studied catalysts are characterized by X-ray diffraction (XRD),  $N_2$ -physisorption, Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Temperature Programmed Desorption with ammonia ( $NH_3$ -TPD).
- The catalytic activity of  $V_2O_5-WO_3/TiO_2$  catalyst doped with silver and/or copper for  $NH_3$ -SCR at low temperature is tested.

## 1.4 Research methodology

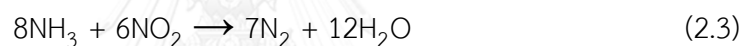
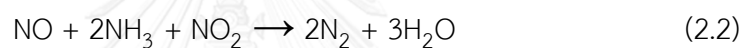
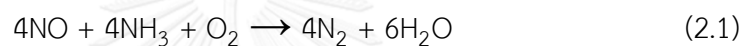


## CHAPTER 2

### THEORY AND LITERATURE REVIEWS

#### 2.1 Selective Catalytic Reduction (SCR)

Selective catalytic reduction is a technology that converts  $\text{NO}_x$  to  $\text{N}_2$  and it is mainly divided into three types which are Standard SCR (2.1), Fast SCR (2.2) and  $\text{NO}_2$  SCR (2.3) [11].



In fact, SCR reaction does not produce  $\text{N}_2$  and water as only product but it also creates unwanted products from several undesirable reactions on the SCR process, which lead to decrease overall conversion of  $\text{NO}_x$  [11-13].

#### 2.2 Catalysts for the SCR process

For the SCR process, the catalysts are based on various supports, such as alumina, silica, zirconia and titania or pure metal including metal oxide, and  $\text{V}_2\text{O}_5\text{-WO}_3$  or  $\text{V}_2\text{O}_5\text{-MoO}_3$  oxides as catalyst component supported on the supports. Additionally,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$  and  $\text{MoO}_3$  give rise to high selectivity in the SCR process when they are supported on  $\text{TiO}_2$  anatase. There are two main reason that why  $\text{TiO}_2$  anatase is a great choice of SCR catalyst. The first reason is stability of sulfates on the  $\text{TiO}_2$  surface is weaker than on other oxides supports, such as  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , and  $\text{TiO}_2$  is only weakly and reversibly sulfated in conditions which approach those of the SCR reaction and



the second reason is the excellent dispersion of vanadium oxide species on  $\text{TiO}_2$  which gives rising of isolated and polymeric vanadyl species [13-16]. In fact,  $\text{V}_2\text{O}_5/\text{TiO}_2$  is unstable because it can convert to be a rutile form which is more thermodynamically stable at any pressure and temperature; however,  $\text{V}_2\text{O}_5$  oxide is active sites of catalyst.  $\text{WO}_3$  and  $\text{MoO}_3$ , as promoter of catalyst, solve a problem of surface loss from anatase-to-rutile phase transformation. In addition,  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst can be found more active, corresponding with selectivity, than  $\text{V}_2\text{O}_5/\text{TiO}_2$  and  $\text{WO}_3/\text{TiO}_2$  [13]. Although  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst is the most commonly used, there are some disadvantages such as the toxicity of vanadium inhabit, the narrow performance windows located at 300-400°C and catalyst deactivation occurring because of ash, alkali oxide,  $\text{SO}_2$  and salt in the flue gas [3, 4, 12, 13].

### 2.3 Other oxide for SCR catalyst

Addition of some transition metals is able to achieve or reduce overall activity of the catalyst indicated that investigation of adding transition metal on  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  is interesting [17-20]. The prices of silver and copper while comparing with other transition metals, it should be concern to study the effect of those metals in oxide form doping with SCR catalyst. Silver species on a catalyst can occur in form of silver ions or ionic silver clusters that active in the SCR of  $\text{NO}_x$  [6]. Although, many researches have focus on silver being active sites of catalyst on various supports such as  $\text{V-Al}_2\text{O}_3$ , ZSM5, ceria-zirconia and zeolite in SCR reaction using hydrocarbon or urea as reducing agent but less literatures concern about silver metal or silver oxide over titania support [6, 21-28]. In case of copper loading on the catalyst, Cu and CuO species tended to enhance the activity and selectivity of SCR catalyst when, especially, the copper species are doped on titania support with co-doping metal and in the condition of low temperature reaction [29, 30]. As described above, silver and copper lead to increase  $\text{NO}_x$  conversion while operate SCR process in low temperature.

## 2.4 Preparation method for catalyst

There are several procedures to prepare or synthesize catalyst; however, this is one of the factors that can affect to physical and chemical overall properties of the catalyst [31]. For instance, the difference surface vanadia state of  $V_2O_5/TiO_2$  catalyst playing an important role in the SCR reaction influence from dissimilar preparation methods. Forming of vanadia species in  $V_2O_5-WO_3/TiO_2$  or  $V_2O_5/TiO_2$  catalyst are isolated vanadyl species and polymeric vanadyl below monomeric surface coverage which is an important reason giving rise activity in the SCR reaction. In case of SCR of  $NO_x$  process, some authors approved with impregnation method that this method was able to form both isolated and polymeric surface  $VO_x$  species appeared with medium vanadium surface coverage resulting in the great performance for the SCR catalyst [13, 32]. On the other hand, some literatures suggested that sol-gel method could be an alternative procedure to synthesize catalyst for  $NH_3$ -SCR of  $NO_x$  at low-temperature because of strong interaction, high surface area, high concentration of hydroxyl groups and great concentration of active sites on catalyst's surface [31, 33, 34]. Even though, debating of catalyst preparation should be concerned, whereas well-known industrial catalyst likes  $V_2O_5-WO_3/TiO_2$  produced from impregnation method. Many authors and literatures believe that this method can make excellent  $V_2O_5-WO_3/TiO_2$  catalyst for operating in industry [13].

## 2.5 Kinetic model for SCR reaction

SCR reaction has been studied under real conditions in many literatures for kinetic researches based on both only mechanistic methods (e.g. Langmuir-Hinshelwood or Eley-Rideal models) and/or empirical expression (e.g. power-law kinetics). Though, various authors subtract the points of mechanistic data from their kinetic models in order to solve them in short. To determine  $NO$  conversion rate from the SCR reaction, the assumption is relied on the reactant concentrations ( $C_{NO}$ ,  $C_{NH_3}$ ,

$C_{O_2}$ ) and as well as concentration of water ( $C_{H_2O}$ ), which presents in the feed under real condition and by-product of SCR reaction, might be concern. Therefore, the supporting empirical power kinetic equation is adapted to reasonable model kinetic information [13].

$$r_{NO} = k_C C_{NO}^a C_{NH_3}^b C_{O_2}^c C_{H_2O}^d \quad (2.4)$$

For pure  $V_2O_5$  and  $V_2O_5/TiO_2$  catalysts working under excess oxygen SCR condition and in absence or presence of water contents above 5%, several authors agree that on vanadia-based catalysts the rate dependency from NO has been estimated to be 1, and ammonia concentration has no effect on reaction then the reaction order with respect to ammonia is zero [35-41]. Therefore, the rate reaction becomes first order.

$$r_{NO} = k_C C_{NO} \quad (2.5)$$

Owing to this kinetic model result, Inomata et al. [68] and most authors noticed that ammonia reacts on a site being a strongly adsorbed state where as NO reacts from the a weakly adsorbed state.

## 2.6 Catalyst behaviors in the reaction between $NH_3$ and NO

Reaction of standard SCR, in typically, NO conversion in SCR condition reaches to be closely total with the ratio of NO and  $NH_3$  to be 1 already near 270 °C, in this case, it seems to imply that the reaction 2.1 appear selectively and  $N_2O$  does not occur in this working window. Evident expectation on SCR process is that on catalysts the standard SCR reaction must be able to compete faster than  $NH_3$  oxidation reactions which many literatures show  $V_2O_5-WO_3-TiO_2$  catalysts present considerable

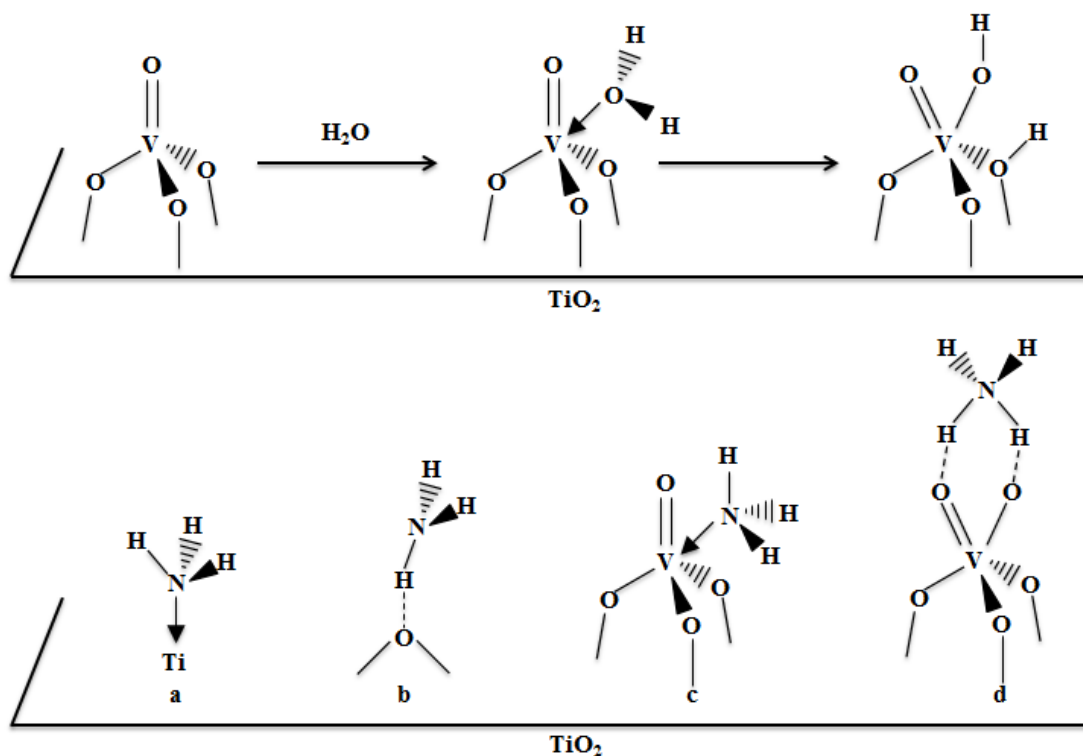
activities for SCR process at temperatures close to 150 °C under excess oxygen feeding condition [11, 13, 33, 42]. On the other hand, the NO conversion reduces clearly at the temperature above those working window because of competition between standard SCR and NH<sub>3</sub> oxidation reactions which both deduct NH<sub>3</sub> from reactant of reaction [43]. For working temperature window on industrial catalyst, NH<sub>3</sub> consumption rapidly occur in the SCR reaction before NH<sub>3</sub> oxidation reaction instead of the competitive reaction. From this point, it indicates that both SCR and NH<sub>3</sub> oxidation reaction have different rate-determining step [13]. NH<sub>3</sub> oxidation reaction is examined in order to explain the complicated chemistry of SCR system which follows the three main reactions as mentioned in Chapter 1 [44].



Factors affected on the SCR catalysts have not only active sites but also those supports. MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> on silica-based catalyst are more active and selective to N<sub>2</sub> than those on titania-based catalyst [45]; however, some research found that the opposite result appears while doping WO<sub>3</sub> [46]. This point implies that support influences in term of chemical and structural of the catalyst site. Ammonia adsorbs on pure V<sub>2</sub>O<sub>5</sub>, on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> in two different massively held species which are Lewis- type interaction on coordinative unsaturated cations and ammonium ions, over Brønsted acidic -OH surface hydroxyl groups [47-49]. Molecular adsorbed NH<sub>3</sub> species are produced on Ti<sup>4+</sup>, vanadyl and wolframyl cations; however, these species cannot be distinguished spectroscopically. In the SCR reaction, ammonia storage is possibly participated to Ti- and W-bound ammonia species, which are

greatly adsorbed on the catalyst surface. On the other hand, these species barely active in the SCR reaction, but they are possibly associated in the SCR reaction upon gas desorption or re-adsorption closing reactive V sites. Hence, Ti— and W—bound ammonia species, which illustrate the main factor of adsorbed ammonia over  $V_2O_5$ - $WO_3$ - $TiO_2$  catalyst, are related in the NO consumption [13].

Busca et al. (1998) presented that V—OH sites from  $V_2O_5/TiO_2$  are vanadyl sites that ammonium ions are formed on those sites which are Lewis acidic and can convert to Brønsted sites by water adsorption [13]. The step of surface species occurring from ammonia adsorption can be displayed on Scheme 2.1, assuming that polymeric vanadates cannot adsorb ammonia because of their coordinative saturated. For  $V_2O_5$ - $WO_3/TiO_2$  catalyst, not only Lewis bonded species on wolframyl species but also Brønsted-bonded  $NH_4^+$  species at W—OH sites are established. In term of thermal stability of  $NH_3$  adsorbed species, ammonium ions are less thermal stable than Lewis bonded molecular species [49-51]. Effect of water competition with ammonia on Lewis acid sites is able to enlarge the amount of Brønsted acid sites; accordingly, it means amount of protonated ammonia species are enhanced [52]. Owing to greater basicity of ammonia, it can demote water from Lewis acid sites.  $NH_3$  strongly adsorbs on vanadia/titania catalysts and on the catalyst surface discovers ammonia surface species having different thermal stability [53]. However,  $NH_3$  adsorption over  $CuO/TiO_2$  catalyst at room or lower temperature cannot detect Brønsted acidity on the surface, yet this catalyst is observed as an active catalyst in the reduction of NO by  $NH_3$ . From this point it can conclude that the Brønsted acidity on the surface does not require for the SCR activity at low temperature [18]. In case of pure  $TiO_2$ , it shows only Lewis acidity and poor catalytic activity for SCR, but Lewis acid sites of titania can be increased by sulfation [54, 55].



**Scheme 2.1** Forming schemes of the Brønsted acid sites from surface vanadyl centers and predicted structures for ammonia adsorbed over  $\text{V}_2\text{O}_5/\text{TiO}_2$ : (a) Lewis-bonded  $\text{NH}_3$  at Ti sites; (b) H-bonded  $\text{NH}_3$  on oxide sites; (c) Lewis-bonded  $\text{NH}_3$  at vanadyl sites; (d) ammonium ions bonded at V Brønsted acid sites.

From theory, NO can adsorb in a molecular form, increasing surface nitrosyls where it interacts with a lone pair of N atom to the surface metal cationic centers, and can be oxidized by oxide surface, increasing some species such as nitrosonium ions ( $\text{NO}^+$ ), nitrite ions ( $\text{NO}_2^-$ ), adsorbed nitrogen dioxide ( $\text{NO}_2$ ), nitronium ion ( $\text{NO}_2^+$ ) and nitrate ions ( $\text{NO}_3^-$ ). Moreover, NO can be reduced to  $\text{NO}^-$  and to its dimeric form as well as to  $\text{N}_2\text{O}$  and  $\text{N}_2$  by itself because NO has an ability to act as an oxidizing agent [56]. For  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst, NO can reoxidize the centers of  $\text{V}_2\text{O}_5$ , which NO adsorbs in form of nitrosyl and dinitrosyl surface species on reduced  $\text{V}_2\text{O}_5$  surfaces, and can also adsorb on  $\text{TiO}_2$  support. These mean that oxidized NO adsorbed species can be

reduced by reduced catalyst center and can be formed on the surface of catalyst too [57]. In case of CuO–TiO<sub>2</sub> and CuO/Al<sub>2</sub>O<sub>3</sub> catalyst, NO adsorbs in various form which these species are able to desorb or decompose at low temperature (<250°C) and mainly give back NO [18, 58]. In addition, the formation of quite stable nitrosyl species with obviously species, containing more oxygen atoms, is not clearly to understand, but these species are indicated as NO<sub>2</sub> or nitrate-like species and also give back NO [59, 60]. The nitroxyl species are act as intermediate in ammonia oxidation to both NO and N<sub>2</sub>O [61].

The co-adsorption of NH<sub>3</sub> and NO on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst is considered that the molecularly adsorbed ammonia species with NO, probably via the amide species, induced to the formation of nitrogen and water as products of reaction, and adsorbed nitrosamide species (NH<sub>2</sub>NO) act as an intermediate of reaction [49, 50]. Ammonia, which is adsorbed on the Brønsted acid sites jointed with V<sup>5+</sup>–OH species, is importantly the SCR reaction. Furthermore, the V=O sites are affected in adsorbed ammonia activation and play a role in the catalytic cycle. However, adsorbed NO species does not occur on the surface of catalyst [62]. NH<sub>3</sub>+NO reaction is carried out at relatively low temperature (<350–400°C) on vanadia/titania catalyst, and two N-atoms, one from NH<sub>3</sub> and another one from NO, are formed nitrogen. Odriozola et al. (1989) suggested that the formation of nitrogen is not control by either NH<sub>3</sub> or NO alone in the SCR reaction because of a mechanism involving the direct coupling between NH<sub>3</sub> and NO [57]. From the results of many authors., these results investigated from NH<sub>3</sub> and NO adsorption–desorption on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst; moreover, these results confirmed that NH<sub>3</sub> is massively associated in adsorption-desorption process on catalyst surface, while NO does not appreciably adsorb on the surface of catalyst [63, 64]. There are various evident that NO cannot adsorb or interact with the surface of vanadia-based catalysts. For example, NO reacts on vanadia- based catalyst,

especially from the gas-phase, and limited bound of V=O oxygen probably blockade NO oxygen atom [65-68]. Besides, the competition between reactant NO and NO decomposition on active sites is involved because oxygen obstruct the decomposition, and  $V_2O_5$  as well as  $WO_3$  do not active in NO decomposition [13, 69]. Therefore, almost catalysts active for ammonia but it hardly active for NO, in particularly under SCR condition with excess oxygen. Lietti et al. (1998) suggested that the performance of  $NH_3+NO$  reaction over catalysts can explained by Lewis-bonded coordinated ammonia in the SCR reaction. They explained that ammonia is activated on Lewis acid sites before reacts with gas-phase NO to produce nitrogen. They also hypothesized that the activated ammonia on the SCR catalysts is formed into amide species and then these species either react with gas-phase NO to produce nitrogen in way of SCR reaction or dimerize to hydrazine, which eventually produce  $N_2$  via the selective oxidation of ammonia [18, 64]. As described above about Ti—, V— and W— sites, Lietti et al. (1998) developed that ammonia can adsorb in those sites in the form of molecularly coordinated  $NH_3$ , but  $NH_4^+$  ions can only be formed on V— and W— sites. Although, ammonia is strongly adsorbed over  $V_2O_5-WO_3/TiO_2$  catalyst, but each sites and species of this catalyst have a different duty in the  $NH_3+NO$  reaction. Not only Ti—sites but V— and W—oxides species act as adsorption sites for ammonia, whereas only V—species primarily act on NO consumption in the process [64]. This point out that on the catalyst surface presents adsorbed ammonia storage, which is available for the SCR reaction; however, ammonia is consumed by gas-phase NO on V—sites only.

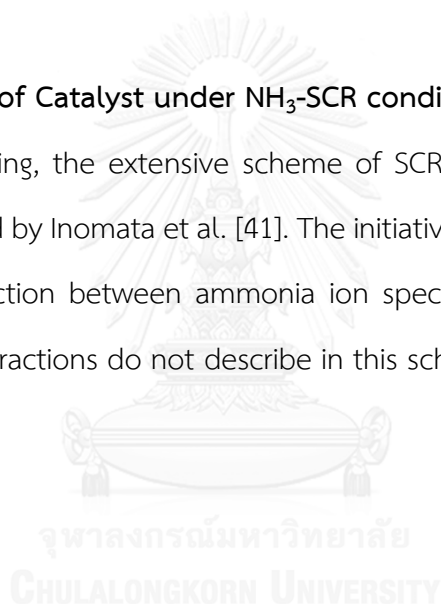
Centi et al. (1995) investigated the performance of  $NH_3+NO$  co-adsorption over  $Cu/Al_2O_3$  catalyst.  $NH_3$  is adsorbed in form of ammonia ions and chemisorbed, but NO is strongly adsorbed over this catalyst surface. This result contrasts to NO adsorbed over vanadia-based catalyst. Additionally, NO adsorption enlarges, in form of nitrate, nitrite and nitrosyl species, in the presence of oxygen; however, NO chemisorption is

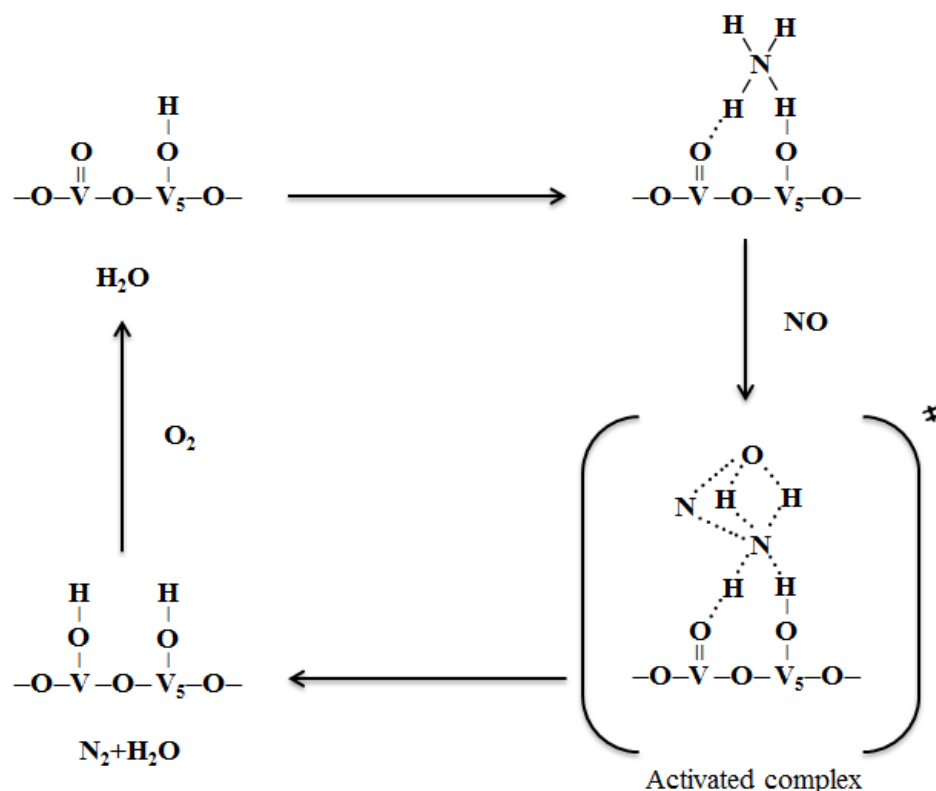


reduced in the presence of ammonia. Transformation of nitrate species, arising from  $\text{NH}_3+\text{NO}$  co-adsorption, might initiate ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which could decompose to generate  $\text{N}_2$  or  $\text{N}_2\text{O}$ . This phenomenon was proved by FTIR experiments of their reaction. It can be concluded that NO is able to originate  $\text{N}_2\text{O}$ , arising from the reduction of NO with ammonia, over  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst. Moreover, Centi et al. suggested that  $\text{Cu}-\text{NH}_2$  species, generated from the splitting of ammonia coordinated on  $\text{Cu}^{2+}$  sites and reacted with NO to produce water and nitrogen, should be considered [70, 71].

## 2.7 The mechanism of Catalyst under $\text{NH}_3$ -SCR condition

At the beginning, the extensive scheme of SCR reaction over vanadia-based catalyst was proposed by Inomata et al. [41]. The initiative scheme, showing in Scheme 2.2, explains the reaction between ammonia ion species and gaseous NO, but the intermediate and interactions do not describe in this scheme.



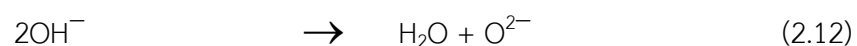
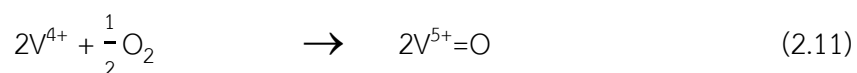
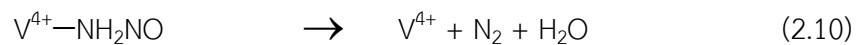
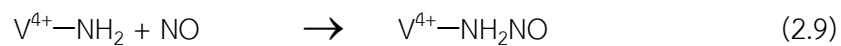
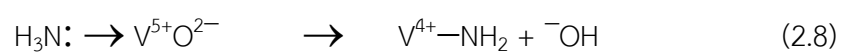
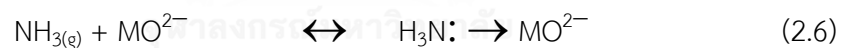


**Scheme 2.2** The mechanism of NO and NH<sub>3</sub> reaction over V<sub>2</sub>O<sub>5</sub> catalyst in the presence of oxygen proposed by Inomata et al. [41].

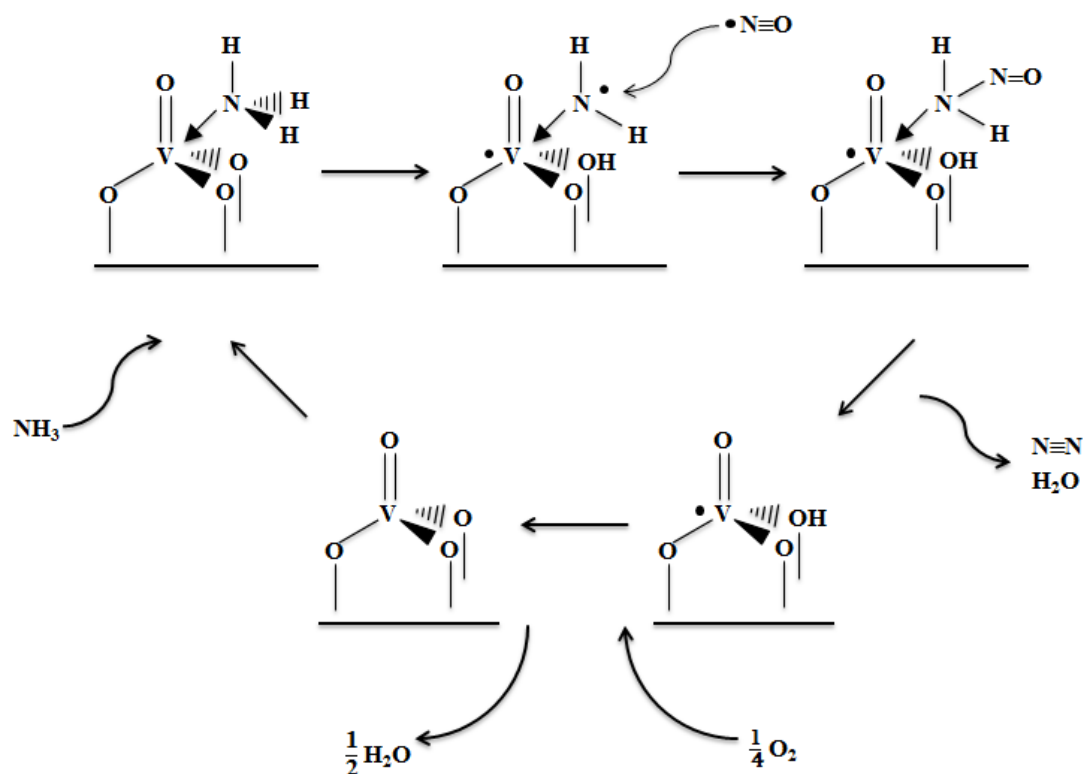
Afterward, several authors offered the key intermediate in the SCR reaction that explained their mechanism. However, almost experiments point out the clue leading to the reliable mechanism that can explain the experimental evident and chemical ground. The “amide—nitrosamide” mechanism is the acceptable one which clarifies the interaction results referring the adsorption-desorption and acidity on catalyst surface from TPSR, TPR, TPD and FT-IR [13, 41, 64, 67, 68, 70-77].

On the basis of kinetic and adsorption data, mentioned above, the agreement mechanistic model relate with the research of Ramis et al. [52]. They investigated the mechanistic model over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst for NH<sub>3</sub>-SCR reaction that show in Scheme 2.3. This mechanism is related with the basis of amide-nitrosamide

mechanism. Firstly, ammonia is adsorbed on the catalyst surface via Ti-, V- and W-sites as well as sulfate species (if they occur in process). This step is the reversible  $\text{NH}_3$  adsorption. These sites are implied similar to Lewis ( $\text{MO}^{2-}$ ) and Brønsted ( $\text{M-OH}$ ) acid sites, but the observation participated only V-bonded molecular adsorbed ammonia. However, Ti- and W-sites on the catalyst surface are also involved in the reaction because ammonia can hold on Lewis and Brønsted sites. Although, Ti- and W-sites can act as “storage” but these sites can be participated in the reaction by the role of “migration”, which reactive V-sites. After ammonia adsorbed on V-sites, amide  $\text{NH}_2$  species are produced over Lewis V acid sites leading to catalyst reduction. Secondly, the activated species react with gas-phase NO providing nitrosamide, which is an intermediate species. Nitrogen and water are generated by the decomposition of nitrosamide. Next, gas-phase oxygen participates to regenerate the reduced catalyst sites. All process that mentioned above summarizes the standard SCR reaction (2.1) and is shown as following steps [52, 64]:



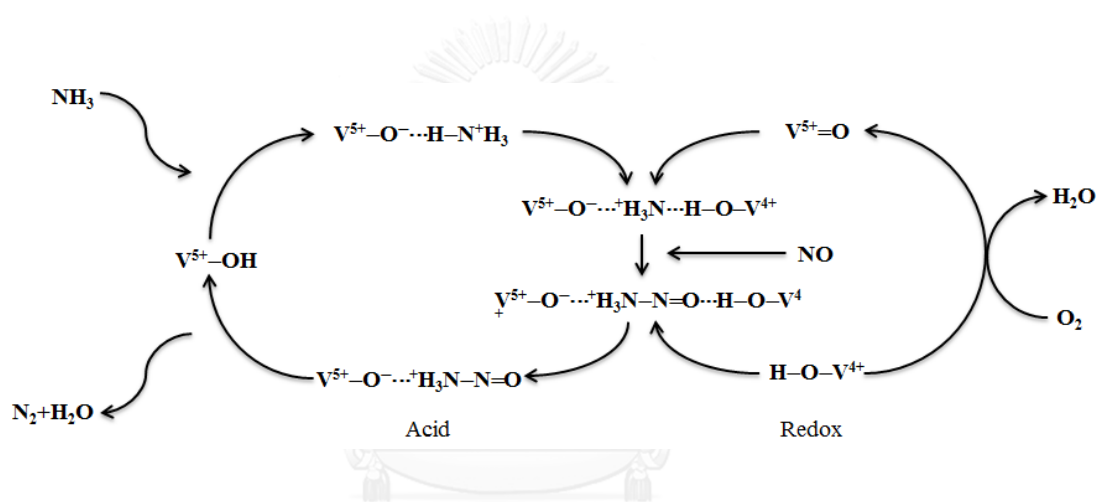
Moreover, this mechanism also explain through Cu-based catalyst, which also proposed by Ramis et al. [18].



**Scheme 2.3** The mechanistic model of  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst under  $NH_3$ -SCR of NO reaction proposed by Ramis et al. [52].

Topsøe et al. (1995) presented the mechanism that describes the correlation of catalytic activity from ammonia adsorbed on the Brønsted acid sites participated with  $V^{5+}$ -OH sites. This mechanistic scheme is shown in Scheme 2.4.  $V^{5+}=O$  group is played a role in activation of adsorbed ammonia by transfer or partial transfer of H from  $NH_3$  molecule in order to produce reduced  $V^{4+}$ -OH sites. The gas-phase NO reacts with the activated ammonia complex resulting in the formation of an intermediate, and then the decomposition are occurred to produce  $N_2$  and  $H_2O$ . Oxygen is associated in the reaction to regenerate the active sites by the oxidation of the reduced  $V^{4+}$ -OH

sites to form  $V^{5+}=O$  group; however, this catalytic cycle consists of both acid-base and redox functions [62]. It should be noted that this mechanistic scheme is an adjustable modification of the mechanism proposed by Ramis et al. [52], in which the Brønsted acid sites are discussed as ammonia adsorption sites instead of Lewis acid sites. Moreover, these authors pointed that  $NH_3^+$  species, produced by extracting an electron from ammonia, would be an intermediate and a radical-cation from their assumption supposing a kinetic role.



**Scheme 2.4** The catalytic cycle of SCR reaction over vanadia/titania catalyst proposed by Topsøe et al. [62].

## CHAPTER 3

### EXPERIMENTAL

This chapter is divided into 3 sections, which are catalyst preparation, characterization of catalyst and catalytic activity testing system, and explains experimental procedures, details in catalytic characterization as well as diagram and analysis system used in selective catalytic reduction of nitrogen oxide by ammonia.

#### 3.1 Catalyst preparation

This section gives details in procedures of catalyst preparation. The used catalysts in this study is presented in Table 3.1.

**Table 3.1** List of catalysts used in this study.

Catalysts symbol	Estimate metal oxide composition (%wt.)			
	V <sub>2</sub> O <sub>5</sub>	WO <sub>3</sub>	Ag <sub>2</sub> O	Cu <sub>2</sub> O
3V7W	3	7	-	-
3V7W2Ag	3	7	2	-
3V7W4Ag	3	7	4	-
3V7W6Ag	3	7	6	-
3V7W2Cu	3	7	-	2
3V7W4Cu	3	7	-	4
3V7W6Cu	3	7	-	6

### 3.1.1 Preparation of titanium dioxide by a sol-gel method

A sol-gel method was used to prepare titanium dioxide by using titanium isopropoxide (Aldrich Chemical, Milwaukee, WI) as a precursor. The method began with 7.33 ml of nitric acid 70 % (Asia Pacific Specialty Chemical Limited) was added to 1,000 ml of deionized water as the acid solution was stirring. Then 83.5 ml of titanium isopropoxide was poured slowly and the suspension appeared. The suspension was stirred continuously until sol became clear. To prepare TiO<sub>2</sub> support powder, TiO<sub>2</sub> sol was dialyzed in a cellulose membrane with a molecular weight cutoff of 3500 (Spectrum companies, Gardena, CA) by deionized water until pH of sol reached a value of 3.3 - 3.5. The dialyzed sol was dried at room temperature and xerogel was obtained. The gel was dried at 110°C overnight, crushed, ground, and then calcined at 350°C for 4 hours.

### 3.1.2 Preparation of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst by incipient wetness impregnation method

Ammonium metavanadate (>99.999%; Aldrich Chemical) was used as a precursor of vanadium to make V<sub>2</sub>O<sub>5</sub> sol by dissolving it into acid solution that made from deionized water and oxalic acid. The yellow clear solution was obtained.

Ammonium metatungstate hydrate (>99.99%; Aldrich Chemical) was used as a precursor of tungsten to make WO<sub>3</sub> sol by dissolving it into deionized water. The clear solution was obtained.

Calculated V<sub>2</sub>O<sub>5</sub> sol dropped onto TiO<sub>2</sub> powder and mixed the powder until they were appeared uniform. After that, the powder was dried at 110°C overnight and then calculated WO<sub>3</sub> sol dropped onto this powder and repeat the same procedure. The powder was calcined at 500°C for 2 hours. Calculation of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> sol are presented in APPENDIX A.

### 3.1.3 Preparation of $V_2O_5$ - $WO_3$ - $TiO_2$ doping with $Ag_2O$ and $Cu_2O$

Silver nitrate (>99.999%; Aldrich Chemical) and Copper nitrate (>99.99%; Aldrich Chemical) were used as a precursor of silver and copper respectively to make  $Ag_2O$  and  $Cu_2O$  sol by dissolving it into deionized water. The clear solution was obtained in case of  $Ag_2O$  sol, and the blue clear solution was appeared in case of  $Cu_2O$  sol.

To prepare  $V_2O_5$ - $WO_3$ - $TiO_2$  doping with  $Ag_2O$  and  $Cu_2O$  in range of 2-6 %wt., the method was incipient wetness impregnation, same as the previously methods. Calculation of  $Ag_2O$  and  $Cu_2O$  sol are presented in APPENDIX A.

## 3.2 Characterization of catalyst

### 3.2.1 Surface area measurement

The specific surface area was determined by nitrogen adsorption method. The single point specific surface area of the catalysts was measured by Micromeritics ChemiSorb 2750 using nitrogen as the adsorbate. The sample weighed about 0.1 g and degassed at 200°C for 1 hour by the ultra high purity nitrogen at a gas flow rate about 15 ml/min. Liquid nitrogen required to cool down the sample, and then measured the TCD signal generated by the adsorption of nitrogen gas which consist of 30% nitrogen in helium. When the TCD signal went stable, the adsorption information was recorded after that the liquid nitrogen was removed to measure the TCD signal generated by desorption. Later the TCD signal became stable, desorption information was noted.



### 3.2.2 X-ray diffraction (XRD)

XRD patterns of catalysts were obtained using SIEMENS D-5000 diffractometer with  $\text{CuK}\alpha$  radiation source. Intensity data was recorded in a  $2\theta$  range from 20 to 80 degree. The crystal structure of catalyst was identified by XRD spectrum. The intensity diffraction peak of XRD patterns, which was estimated from the half-height width of the highest by Debye-Scherrer equation, was used to calculate crystallite sizes of catalysts.

### 3.2.3 Estimation of composition of catalyst using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Inductively-coupled plasma optical emission spectroscopy (ICP-OES) was carried out to determine the percentage of metal loading of each catalyst prepared. About 0.02 g of catalyst was dissolved in the mixed solution between amount of 2.8 g ammonium sulfate and 7 ml sulfuric acid 95%, stirred and heated until all solid were solution then make volume up to 100 ml using deionized water.

### 3.2.4 Temperature programmed desorption ( $\text{NH}_3$ -TPD)

Temperature programmed desorption (TPD) using ammonia as a probe molecule operated in a Micromeritic ChemiSorb 2750 automated system controlled with ChemiSoft TPx software. The amount of ammonia adsorbed and desorbed on surface was measured by thermal conductivity detector (TCD). Temperature-controlled furnace applied to control the operating temperature system. The TCD signal was recorded every second and stored on a computer.

About 0.1 g of sample was placed over quartz wool in glass tube. Ultra high purity helium gas at a flow rate 25 mL/min flowed through and heated the sample from room temperature to 500°C with a heating rate of 10°C/min and held for an hour in order to remove moisture. The sample was cooled down to 100 °C then 15 %vol.

of  $\text{NH}_3$  in helium gas was flowed through sample with a flow rate of 25 mL/min, and held this process for an hour. Afterward, helium gas was fed through the sample until baseline was steady after that the sample was heated to 500 °C with the same heating rate.

### 3.3 Catalytic activity testing system

To measure the catalytic activity, 7 mm ID stainless tubular fixed bed reactor was employed. All catalysts in this study were tested by passing feed gas stream through the catalyst bed packing on quartz wool with 0.1 g of catalyst.

SCR reaction condition for testing activity:

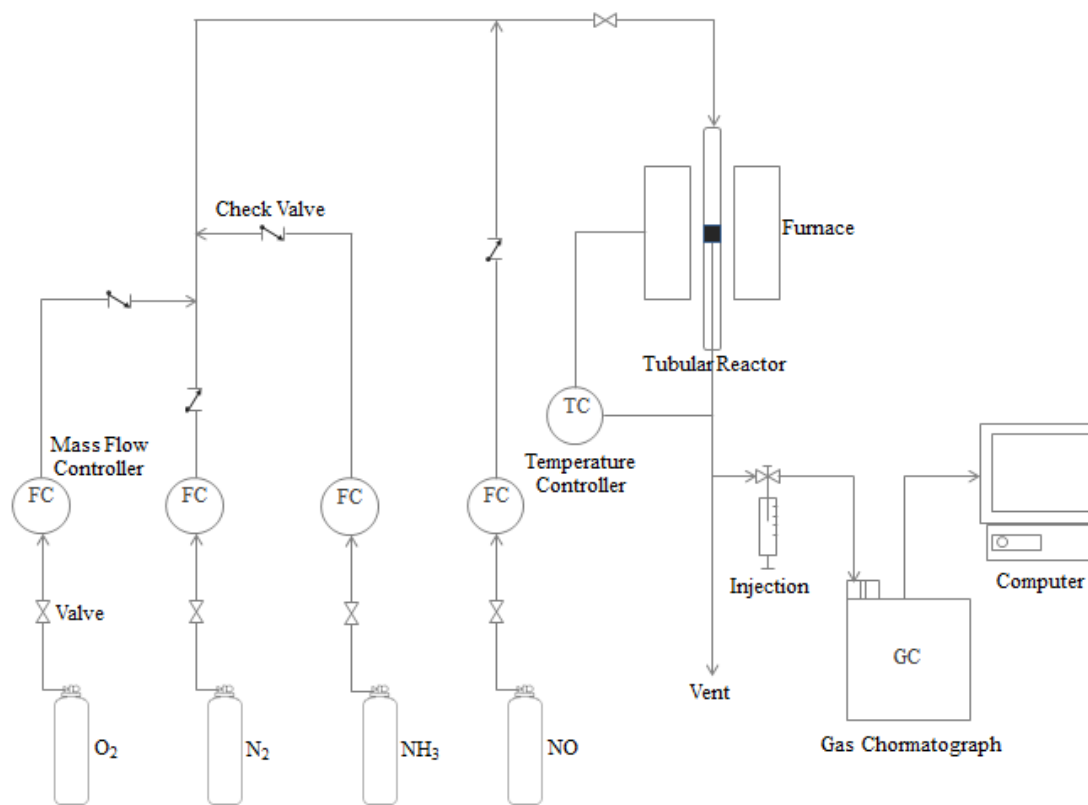
Range of reaction temperature	120 - 400°C
Operation pressure	1 atm
Weight hourly space velocity	120,000 mL/g-hr

Component of feed gas mixture:

$\text{NO}$	120 ppm
$\text{NH}_3$	120 ppm
$\text{O}_2$	15 %vol.
$\text{N}_2$	balance

System temperature was controlled by a digital temperature controller and total flow rate of feed gas mixture approximated 200 mL/min. Each of the feed gas streams was controlled by mass flow controller. And NO concentration was measured by sampling

the product at the outlet stream and analyzed by gas chromatography (GC, SHIMADZU). The diagram of the process is exhibited schematically in Figure 3.1.



**Figure 3.1** Flow diagram of the reactor system for SCR of NO by NH<sub>3</sub>

Step of experimental procedure for reduction of NO with NH<sub>3</sub> is described to the following step.

1. About 0.1 g of catalyst was placed with the bed packing of quartz wool in stainless tubular fixed bed reactor.
2. NO, O<sub>2</sub> and N<sub>2</sub> gas was fed through sample at the ambient temperature, and NO was measured in this step as an initial value.

3. After that, the sample was heated to 120°C and NH<sub>3</sub> gas was fed through sample. NO was measured after holding this condition for 20 minutes to prove the steady-state condition.
4. The sample was heated to 150°C, and NO was measured after holding the temperature for 20 minutes to prove the steady-state condition.
5. The sample was heated by step-change with 50°C until to 400°C. At each temperature, NO was measured after holding the temperature for 20 minutes to prove the steady-state condition.

Step of experimental procedure for NH<sub>3</sub> oxidation is described to the following step.

1. About 0.1 g of catalyst was placed with the bed packing of quartz wool in stainless tubular fixed bed reactor.
2. NO, O<sub>2</sub> and N<sub>2</sub> gas was fed through sample at the ambient temperature, and NO was measured in this step as an initial value.
3. After that, the sample was heated to 120°C. NH<sub>3</sub> gas was fed through sample, while NO was shut down in the process. NO was measured after holding this condition for 20 minutes to prove the steady-state condition.
4. The sample was heated to 150°C, and NO was measured after holding the temperature for 20 minutes to prove the steady-state condition.
5. The sample was heated by step-change with 50°C until to 400°C. At each temperature, NO was measured after holding the temperature for 20 minutes to prove the steady-state condition.

## CHAPTER 4

### RESULTS AND DISCUSSIONS

This chapter includes with the characterization and activities results of the  $V_2O_5$ - $WO_3$ - $TiO_2$  catalyst and promoted catalysts. The results and discussions are separated into 2 sections. The first section discusses characterization of each catalyst, and the second section discusses the selective catalytic reduction of nitrogen oxide by ammonia.

#### 4.1 Catalytic characterization

This section describes the results of characterization for  $V_2O_5$ - $WO_3$ - $TiO_2$ ,  $Ag_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$ , and  $Cu_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts. Characterization techniques using in this work were  $N_2$ -physisorption to determine the specific surface area of the catalysts, X-ray diffraction to identify crystal structures, inductively coupled plasma-optical emission spectroscopy to verify the metal loading, X-ray photoelectron spectrometer to analyze oxidation states of various metals on catalyst surface and temperature programmed desorption using ammonia in order to examine amounts of acid sites on the catalyst surface.

##### 4.1.1 Composition of metal oxides contained in studied catalysts

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was employed to examine the contents of metal oxides such as vanadium oxide, tungsten oxide, silver oxide and copper oxide. About 0.02 g of sample was dissolved in the mixed solution between amount of 2.8 g ammonium sulfate and 7 ml sulfuric acid

95%, stirred and heated until all solid were solution then make volume up to 100 ml using deionized water. Catalyst compositions are reported in Table 4.1 and Table 4.2.

**Table 4.1** The composition of metal oxide contained in  $V_2O_5$ - $WO_3$ - $TiO_2$  and  $Ag_2O$ -doped  $V_2O_5$ - $WO_3$ - $TiO_2$  catalysts

Sample	$V_2O_5$ content (%wt.)		$WO_3$ content (%wt.)		$Ag_2O$ content (%wt.)	
	Proposed	Actual	Proposed	Actual	Proposed	Actual
3V7W	3.0	3.2	7.0	7.2	-	-
3V7W2Ag	3.0	3.1	7.0	7.0	2.0	2.2
3V7W4Ag	3.0	3.1	7.0	7.3	4.0	4.1
3V7W6Ag	3.0	3.1	7.0	7.1	6.0	6.4

**Table 4.2** The composition of metal oxide contained in  $V_2O_5$ - $WO_3$ - $TiO_2$  and  $Cu_2O$ -doped  $V_2O_5$ - $WO_3$ - $TiO_2$  catalysts

Sample	$V_2O_5$ content (%wt.)		$WO_3$ content (%wt.)		$Cu_2O$ content (%wt.)	
	Proposed	Actual	Proposed	Actual	Proposed	Actual
3V7W	3.0	3.2	7.0	7.2	-	-
3V7W2Cu	3.0	3.0	7.0	7.2	2.0	2.3
3V7W4Cu	3.0	3.0	7.0	6.8	4.0	4.3
3V7W6Cu	3.0	3.0	7.0	7.6	6.0	6.5

This result showed that the vanadium oxide contained in all studied catalysts were comparable to the metal content in the preparation. The actual content of tungsten oxide in the catalysts were comparable to the determination except for 3V7W6Cu, which increased from 7.0% to 7.6%. The silver oxide contained in the catalysts were

comparable to the calculation. While the copper oxide actual content in the catalysts increased from 6.0% to 6.5% in case of 3V7W6Cu.

#### 4.1.2 X-ray diffraction (XRD)

Crystal structures of catalysts was studied by X-ray diffraction (XRD) technique. XRD patterns of numerous catalysts including  $V_2O_5$ - $WO_3$ - $TiO_2$  catalyst (3V7W), varied loading  $Ag_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts and varied loading  $Cu_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts are displayed in Figure 4.1.

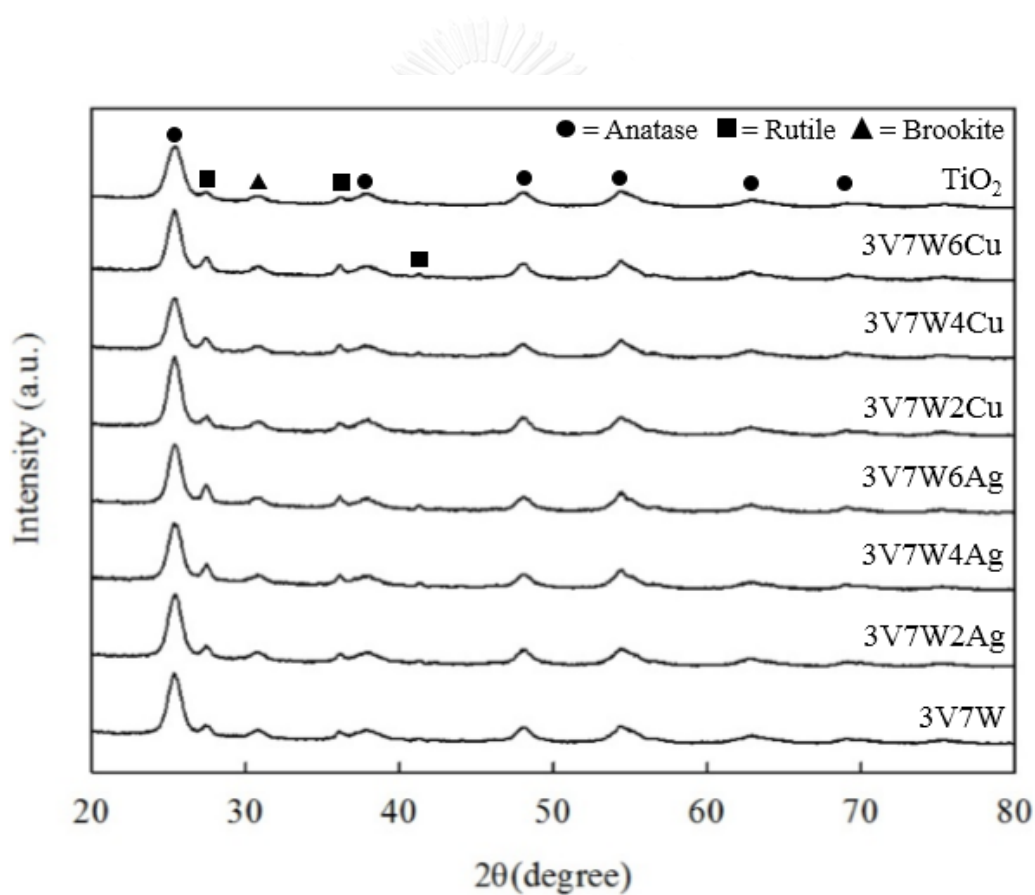


Figure 4.1 XRD patterns of  $TiO_2$  support and catalysts

It is well known that there are three crystallographic phases of  $TiO_2$  discovering in nature that are anatase, rutile and brookite. Though,  $TiO_2$  anatase has essence in SCR reaction because of its high surface area [78]. The predominant phase of catalysts was

anatase  $\text{TiO}_2$  phase. The  $\text{TiO}_2$  anatase main peaks were located at  $2\theta$  of 25.3°, 37.8°, 47.9°, 53.6°, 55.3°, 62.4° and 70.3°. Not only rutile appeared and located at  $2\theta$  of 27.5°, 36.1° and 41.2° degrees but also brookite occurred at  $2\theta$  of 30.7° [79-81]. The XRD patterns suggested that the majority phase of  $\text{TiO}_2$  in all catalysts occurred anatase while the amount of rutile and brookite were also presence [78, 82, 83]. For brookite phase, no substitution obviously found after loading of vanadium, tungsten, silver and copper. No peak of  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{Ag}_2\text{O}$  and  $\text{Cu}_2\text{O}$  crystal structure occurred; therefore, it might be indicated that well dispersion of vanadium, tungsten, silver and copper on the catalysts occurred. On the other hand, vanadium, tungsten, silver and copper loaded on the catalyst were too small so as to detect the phase of crystalline from the technique detection limit [82, 84]. According to the literature reviews, the catalyst with combination of vanadium and tungsten presented enhancing of anatase phase, which was compared with  $\text{TiO}_2$  support, because the promotion of tungsten prevented the problem of surface loss from anatase-to-rutile phase transformation [13]. This contrasted with the catalysts with loading of silver or copper, these catalysts measurably exhibited the increasing of rutile phase.



#### 4.1.3 Specific Surface area of TiO<sub>2</sub> support and studied catalysts

Specific surface area of each catalyst was determined by N<sub>2</sub>-physisorption. The single point specific surface area of the catalysts was measured by Micromeritics ChemiSorb 2750 using nitrogen as the adsorbate. The results are shown in Table 4.3.

**Table 4.3** Specific surface area of TiO<sub>2</sub> support and studied catalysts.

Catalysts symbol	Surface area (m <sup>2</sup> /g)
TiO <sub>2</sub>	83
3V7W	59
3V7W2Ag	53
3V7W4Ag	47
3V7W6Ag	46
3V7W2Cu	47
3V7W4Cu	51
3V7W6Cu	53

The specific surface area of studied V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> (3V7W) catalyst was 59 m<sup>2</sup>/g related to the review of Busca et al. (2005), which reported that the overall surface area of commercial V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst, which is contained by TiO<sub>2</sub> anatase support and impregnated by both V<sub>2</sub>O<sub>5</sub> in range of 0.5-3.0%wt. and WO<sub>3</sub> in range of 5-10%wt. as a monolayer, is around 50 to 100 m<sup>2</sup>/g [72]. The specific surface area of vanadium containing catalyst reduced from 83 to 59 m<sup>2</sup>/g, comparing with bare TiO<sub>2</sub> support, because of anatase-to-rutile phase transformation which favors in the presence of V<sub>2</sub>O<sub>5</sub> with TiO<sub>2</sub> [3]. Furthermore, Addition of metal oxide loading tended to decrease the specific surface area of the catalyst, compared with TiO<sub>2</sub> support, because the impregnated metal oxide cause the plugging effect of the TiO<sub>2</sub> support pores [83, 84]. For Ag<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts, the specific surface area led to slightly

decrease with increasing loading of silver oxide because silver nanoparticles may obstruct the TiO<sub>2</sub> pores, or at the TiO<sub>2</sub> surface may occur Ag-coating [85, 86]. For Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts, these specific surface areas tended to increase slightly from 47 to 53 m<sup>2</sup>/g with increasing loading of copper oxide because the catalyst structure might be changed by the addition of copper oxide [87]. However, it should be noted that the addition of silver and copper oxides over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts did not significantly change of specific surface area.

#### 4.1.4 Surface acidity of studied catalysts

Concentration of acid sites over surface of the catalysts was examined by temperature programmed desorption using ammonia as a probe molecule. The amount of the acid site can be determined from NH<sub>3</sub> which desorbs from the sample. Temperature programmed desorption profiles of all catalysts, obtained in temperature range of 100-500°C, are displayed in APPENDIX B. The amounts of acid sites were determined from the area under the curve of NH<sub>3</sub>-TPD profiles, and these results are reported in Table 4.4.

**Table 4.4** Total acid sites of studied catalysts

Catalysts symbol	Total acid site (mmol NH <sub>3</sub> /g)
3V7W	12.9
3V7W2Ag	11.5
3V7W4Ag	9.3
3V7W6Ag	8.9
3V7W2Cu	14.5
3V7W4Cu	12.3
3V7W6Cu	14.4

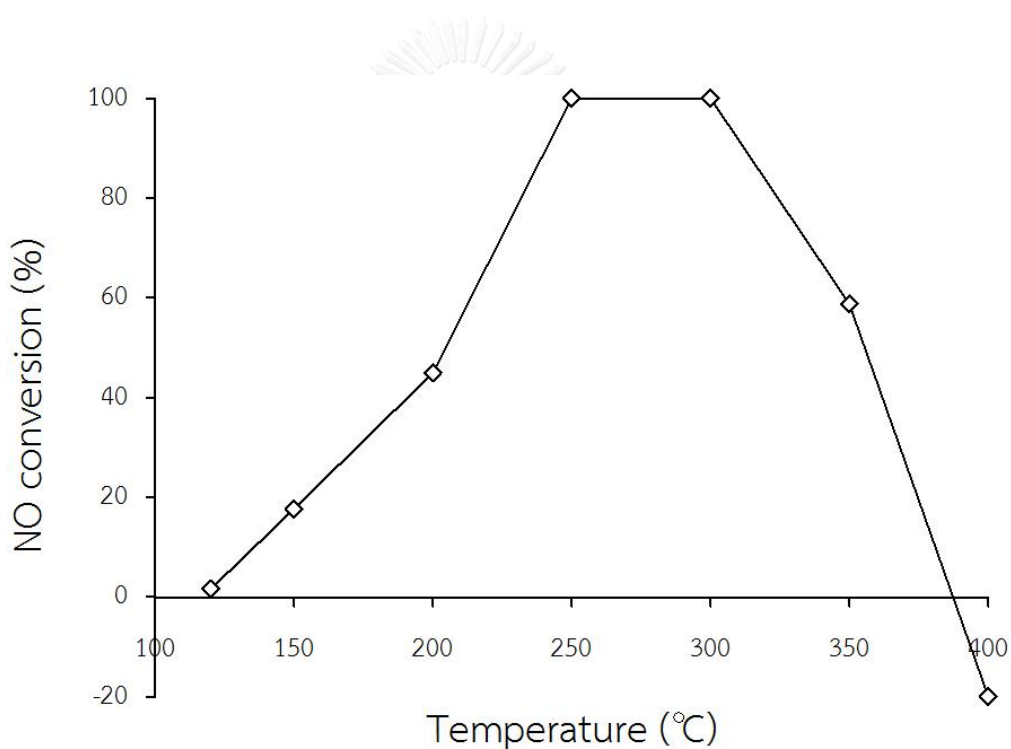
The surface acidity of 3V7W catalyst was 12.9 mmol NH<sub>3</sub>/g. The addition of silver oxide significantly reduced the surface acidity of catalyst from 12.9 to 11.5, 9.3 and 8.9 mmol NH<sub>3</sub>/g. These results were similar to the studied case of Fogel et al. (2012), which reported that adsorption of ammonia reduced with enhancing of silver loading because of silver blocking ammonia adsorption acid sites on the support [28]. On the other hand, the addition of copper oxide significantly increased the surface acidity of catalyst from 12.9 to 14.5 and 14.4 mmol NH<sub>3</sub>/g except 3V7W4Cu catalyst, which slightly decreased the surface acidity of catalyst from 12.9 to 12.3 mmol NH<sub>3</sub>/g. These results implied that the addition of copper might increase the concentration and acidity of acid sites [12]. Wang et al. reported that the amount of Brønsted acid site decreased with increasing copper loading, while the number of Lewis acid sites on the catalyst increased [88].

#### 4.2 Selective catalytic reduction of nitrogen oxide by ammonia

In this section, the activity testing system and condition were previously mentioned in section 3.3, catalytic activity was studied as a function of reaction temperature, and then reported as NO conversion with reaction temperature in range of 120-400 °C. The NO conversion, reported as percentage, in SCR reaction activity generally occurs as same as volcano-type shape [3]. According to the literature reviews, the SCR activity of the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst depends on various factors such as crystalline phase, the specific surface area, and the surface acidity. It is well known that the surface acidity of catalysts always plays an essential role in the SCR of NO<sub>x</sub> by NH<sub>3</sub> because the adsorption of ammonia over the surface of catalyst is one of the most important step for NH<sub>3</sub>-SCR [10, 13, 72, 89].

#### 4.2.1 NH<sub>3</sub>-SCR activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst

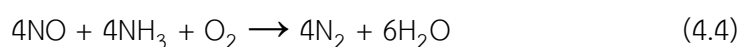
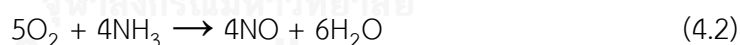
The catalytic activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was tested by approximate 0.1 g of catalyst under the condition: WHSV = 120,000 mL/g·hr, [NO] = [NH<sub>3</sub>] = 120 ppm, [O<sub>2</sub>] = 15%V/V, balance N<sub>2</sub>, total flow rate 200mL/min. Figure 4.2 presents the catalytic activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst.



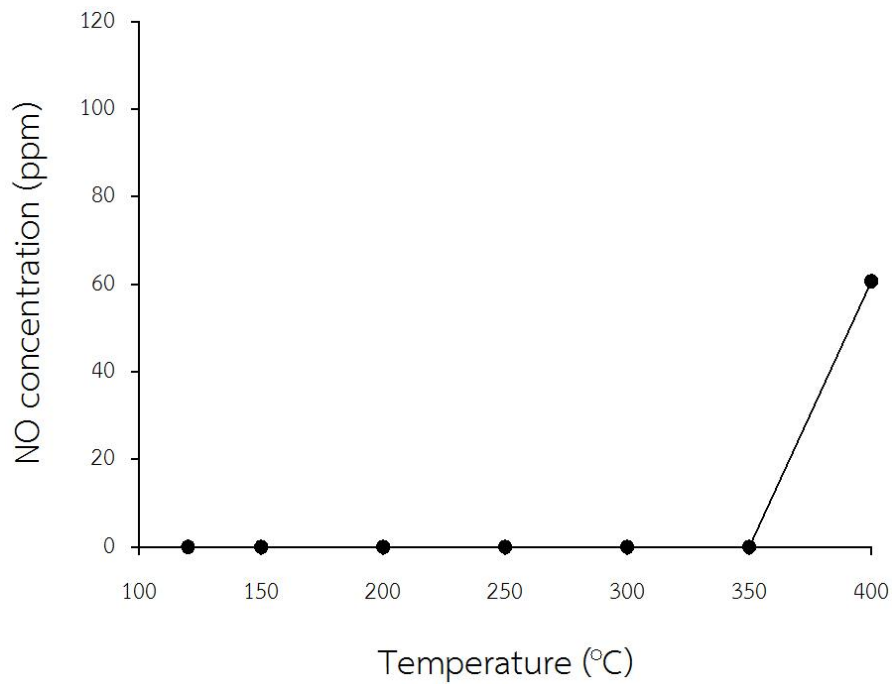
**Figure 4.2** Catalytic activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst for NH<sub>3</sub>-SCR reaction

The NO conversion was poor at the beginning of the reaction and then increased, when the reaction temperature was raised. This catalyst had 100% NO conversion at temperatures between 250°C and 300°C. Nevertheless, the activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst fell to 59% NO conversion at 300°C, and the negative conversion was found

at 400°C with -20% NO conversion. This results can be illustrated by NH<sub>3</sub> oxidation as that explained in the literature reviews. The standard SCR reaction occurred at the temperature around 120°C and raised the NO conversion to the maximum value, and then the NO conversion was dropped by the NH<sub>3</sub> oxidation [3, 13]. A reduction of NO conversion can be discussed by observation of side-reactions (Equation 4.1-4.3), which compete with the main reaction (Equation 4.4) to consume reactant and produce undesirable product. NH<sub>3</sub> is used in NH<sub>3</sub> oxidation, which influences to the lack of NH<sub>3</sub> in the standard SCR reaction resulting in NO in the process does not use to react the main reaction. The remained NO, which obtained from prevention of the SCR reaction (Equation 4.4) by the competition of side reaction, and NO generated from the Equation 4.2 might raise the overall NO in the process more than the reactant value. It is well known that V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts are active in the SCR reaction as well as NH<sub>3</sub> oxidation at higher temperature than those corresponding to the SCR reaction [3, 13]. It was clearly to discuss that why the negative conversion appeared.



The influence of NH<sub>3</sub> oxidation on the catalytic activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was tested under the condition: WHSV = 120,000 mL/g-hr, [NH<sub>3</sub>] = 120 ppm, [O<sub>2</sub>] = 15%V/V, balance N<sub>2</sub>, total flow rate 200mL/min without NO in the feed stream. The result was presented with the function of temperature in range of 120-400°C and shown in the Figure 4.3.

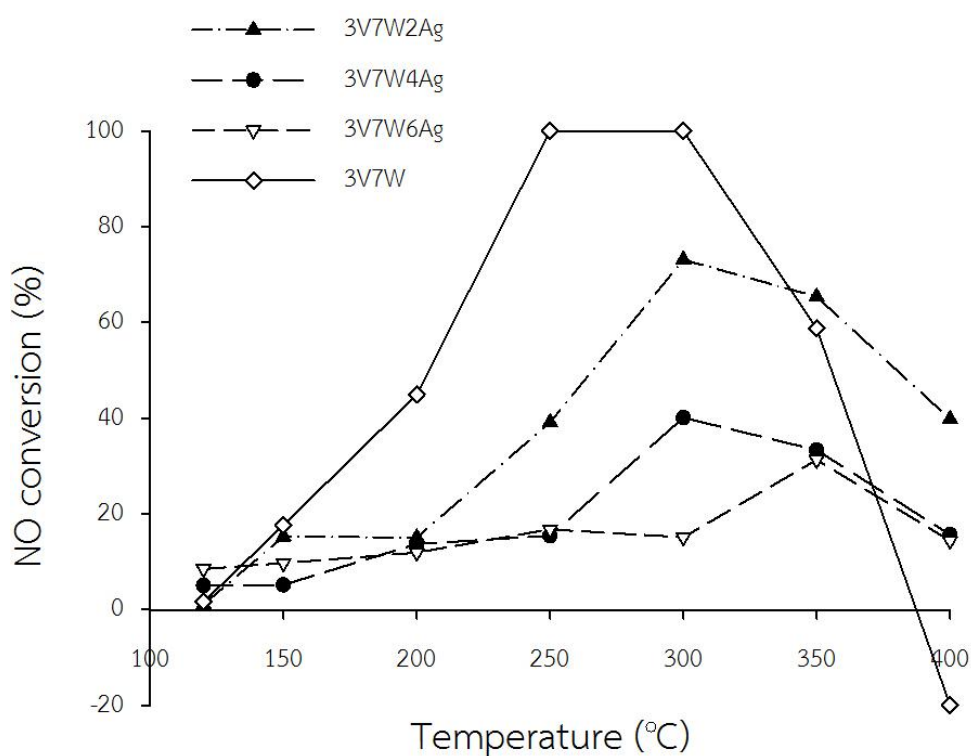


**Figure 4.3** NH<sub>3</sub> oxidation of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst

As shown in the Figure 11, NO only generated from NH<sub>3</sub> oxidation was 60 ppm at 400°C, while NO did not occur at the temperature below 400°C. This confirmed that the negative conversion could appear at 400°C. It might be discussed that NO conversion at 350°C might decrease via Equation 4.1 and 4.3. While Equation 4.1 produced the undesirable product (N<sub>2</sub>O), Equation 4.3, which is called selective catalytic oxidation of ammonia (SCO) process, provided the desirable product (N<sub>2</sub>). Several catalysts which active in the SCR process also active in SCO process even though at slightly high temperature [13].

#### 4.2.2 Effect of silver doping on $\text{NH}_3$ -SCR activity of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst

The catalytic activity of  $\text{Ag}_2\text{O}$ -doped  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst was tested by approximate 0.1 g of catalyst under the condition: WHSV = 120,000 mL/g-hr,  $[\text{NO}] = [\text{NH}_3] = 120$  ppm,  $[\text{O}_2] = 15\%$ V/V, balance  $\text{N}_2$ , total flow rate 200mL/min. The catalytic activities of  $\text{Ag}_2\text{O}$ -doped  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts are directly compared and shown in Figure 4.4.



**Figure 4.4** Comparison of catalytic activity for  $\text{NH}_3$ -SCR reaction by different loading of silver over  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst

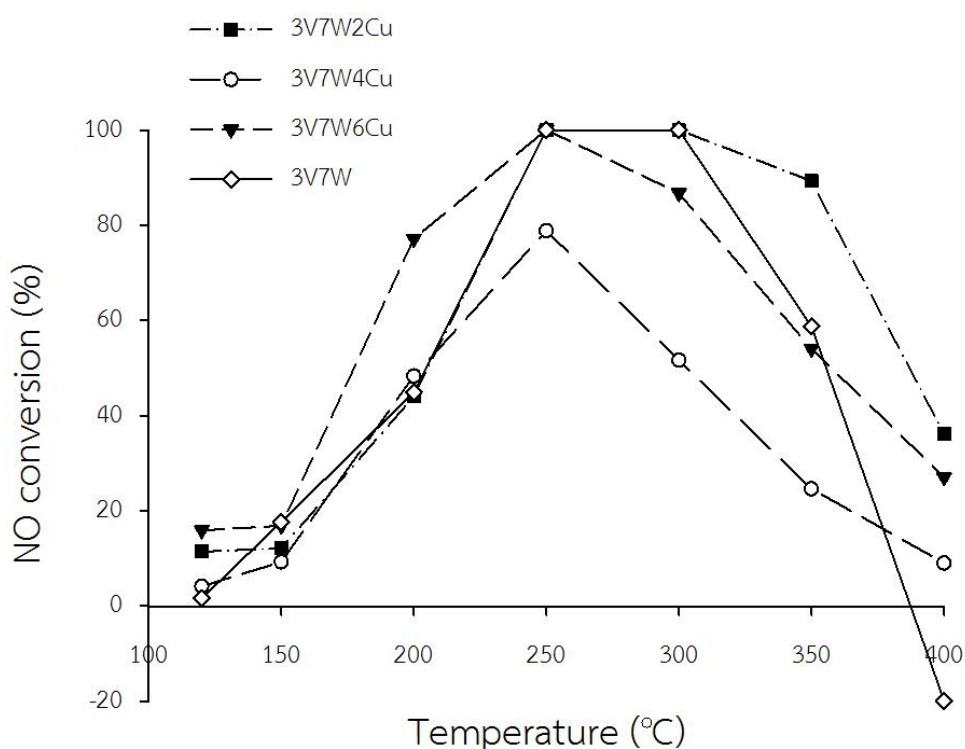
The  $\text{Ag}_2\text{O}$  with 2 and 4%wt. containing over  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts obtained the maximum conversion (73% and 40% NO conversion respectively) at 300°C and then dropped, whereas 6%wt.  $\text{Ag}_2\text{O}$  doped  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst gave the maximum conversion (31% NO conversion) at 350°C. Although, the activities of the catalysts

enhanced with increasing the reaction temperature, but these catalysts offered the inferior NO conversion at low temperature comparing to 3V7W catalyst. Moreover, catalytic activities of the catalysts were significantly decreased with the higher of silver loading, especially, at 250-300°C. Indeed, this explanation is also in line with previous characterization studies presenting that Ag<sub>2</sub>O addition decreased the specific surface area and surface acidity of those catalysts. These results did not agree with those reported in the work of Fogel et al. (2012) [28]. Their study positively presented that catalytic activity at low temperature was large when the 2%wt of Ag loaded on alumina. It might be illustrated that the addition of silver exhibited positive results over Al<sub>2</sub>O<sub>3</sub> while it showed negative results over TiO<sub>2</sub>. It should be noted that a kind of support plays an important role in catalytic activity on NH<sub>3</sub>-SCR reaction [90]. 3V7W2Ag seemed to be better catalyst than the others exploring from catalyst performance. The catalyst performance of Ag<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts was agreed with the total acid sites of these catalysts. The more acid sites presented, the more activity obtained. However, Ag<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts proposed low surface acidity as well as poor NO removal efficiency.



#### 4.2.3 Effect of copper doping on NH<sub>3</sub>-SCR activity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst

The catalytic activity of Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was tested by approximate 0.1 g of catalyst under the condition: WHSV = 120,000 mL/g-hr, [NO] = [NH<sub>3</sub>] = 120 ppm, [O<sub>2</sub>] = 15%V/V, balance N<sub>2</sub>, total flow rate 200mL/min. NH<sub>3</sub>-SCR activities of Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were tested, and the results are reported in Figure 4.5.

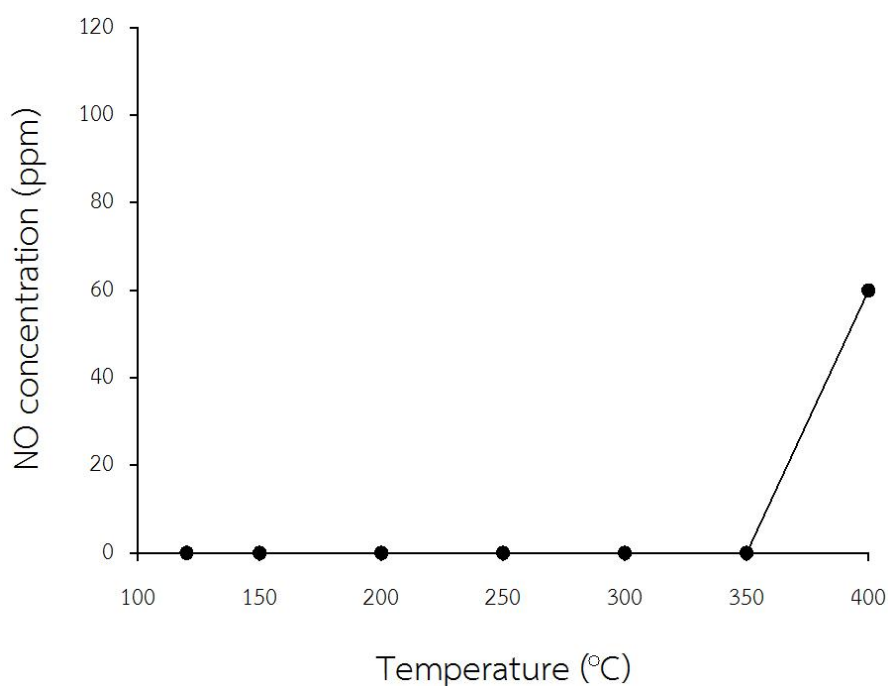


**Figure 4.5** Comparison of catalytic activity for NH<sub>3</sub>-SCR reaction by different loading of copper over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst

NO conversion of the Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were raised by increasing temperature. These catalysts had maximum NO conversion, which was 100% NO conversion for 3V7W2Cu and 3V7W6Cu and 78% NO conversion for 3V7W4Cu, at 250°C, but 3V7W2Cu catalyst performed its activity to 300°C. After appearance of the

maximum NO conversion, NO conversion of Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts were dropped. It can be seen that the similar activation between 3V7W and 3V7W2Cu catalysts was observed until at 300°C. Nevertheless, NO conversion of these catalysts significantly differed when the temperature was above 300°C. Cu<sub>2</sub>O with 2%wt. loading over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst showed well performance comparing to 3V7W catalyst by increasing NO conversion from 58% to 90% at 350°C and -20% to 36% at 400°C. Shape of catalytic activities tended to be the same in case of 3V7W4Cu and 3V7W6Cu catalysts, while 3V7W2Cu catalyst had different activity from those behaviors. In addition, enhancement of Cu<sub>2</sub>O loading from 4%wt. to 6%wt. exhibited improvement of the catalytic activity. In case of 3V7W and 3V7W6Cu catalysts, NO conversion at 200°C increased from 40% to close to 80% when copper oxide was contained. This contrast was considered that there are obvious trends in two different temperature regions for the relationship between copper loading and NO removal efficiency. For the low temperature region (at 120°C), NO conversion enhanced with high copper oxide loading, whereas NO conversion enhanced with low loading of copper oxide in the high temperature region (at 350-400°C). These results agreed with the study of Wang et al. (2014) [88]. Those authors explained that the isolated Cu species are active sites of SCR at low temperature while the Cu<sub>x</sub>O<sub>y</sub> clusters could activate NH<sub>3</sub> oxidation at high temperature. Furthermore, the addition of copper oxide might adjust the dispersion of active sites, which are vanadium species, in the catalyst [87]. In case of 3V7W4Cu, the NO removal efficiency was poor when compared with the others. This can be discussed with the NH<sub>3</sub>-TPD results. Surface acidity is related to the activity of NH<sub>3</sub>-SCR, and 3V7W4Cu catalyst showed the less total acid sites in terms of copper loading over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst. Though, 3V7W4Cu catalyst presented the specific surface area more than 3V7W2Cu, but this result was slight when compared to the total acid sites result. This point supported the idea that surface acidity is the major factor on the NH<sub>3</sub>-SCR reaction.

In order to investigate the effect of  $\text{NH}_3$  oxidation on  $\text{Cu}_2\text{O}$ -doped  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  catalysts, testing condition was similar to the condition that used with  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  catalyst by the absence of  $\text{NO}$  in the feed stream. Figure 4.6-4.8 show the results for 3V7W2Cu, 3V7W4Cu and 3V7W6Cu respectively.



**Figure 4.6**  $\text{NH}_3$  oxidation of 3V7W2Cu catalyst

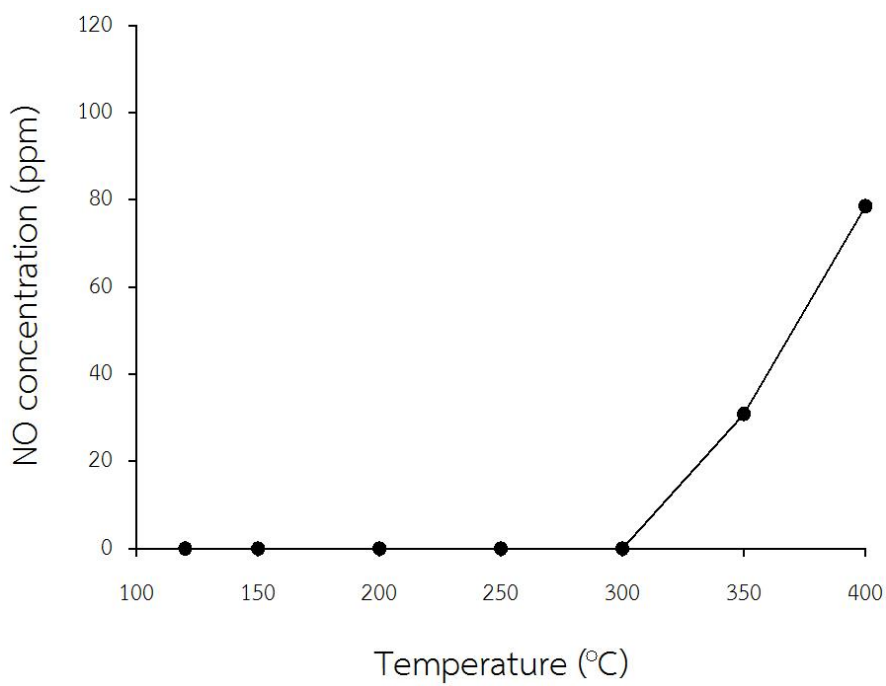


Figure 4.7 NH<sub>3</sub> oxidation of 3V7W4Cu catalyst

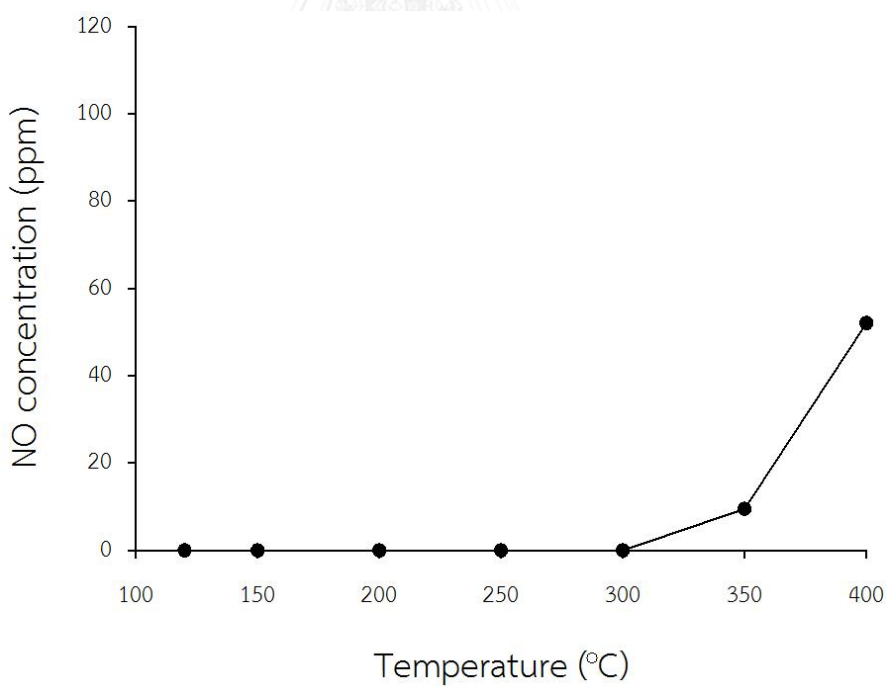
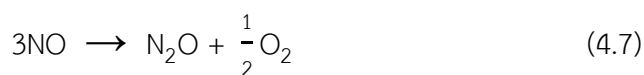


Figure 4.8 NH<sub>3</sub> oxidation of 3V7W6Cu catalyst

For 3V7W2Cu catalyst, NO only generated at 400°C, while appearance of NO at 350°C was found in cases of 3V7W4Cu and 3V7W6Cu catalyst. For 3V7W2Cu catalyst, the influence of NH<sub>3</sub> oxidation occurred at 400°C while NO conversion initiated to drop at 350°C. For 3V7W4Cu as well as 3V7W6Cu catalyst, decreasing of NO conversion was found at 300°C, whereas the effect of NH<sub>3</sub> oxidation presented at 350°C. As mentioned in the section 4.2.1, these might be discussed that NH<sub>3</sub> oxidation by Equation 4.1 and SCO reaction (Equation 4.3) consumed NH<sub>3</sub> in the process hindering the standard SCR reaction. NH<sub>3</sub> oxidation (Equation 4.1-4.3) are also parallel to the standard SCR reaction (Equation 4.4) at high temperature because of thermodynamic stability of products, which are N<sub>2</sub>, N<sub>2</sub>O and NO [13]. Although, these results demonstrated that copper oxide was also active in NH<sub>3</sub> oxidation reaction, surprisingly, the negative conversion did not appear for Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts, while high NO concentration was found. It might be discussed by the production of N<sub>2</sub>O at high temperature. N<sub>2</sub>O can arise from NO without ammonia in reaction (Equation 4.6-4.7); however, the catalysts, which active in SCR reaction, can also active on the decomposition of N<sub>2</sub>O (Equation 4.8) [11, 13].



Additionally, these results could imply that reaction of NH<sub>3</sub> can appear over the surface of Cu<sub>2</sub>O, which should be the active sites for NH<sub>3</sub> oxidation [10, 29].

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

The conclusions, which provided throughout the experimental results, and the recommendation for further study is also given in this chapter.

#### 5.1 Conclusions

A series of  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst with various  $Ag_2O$  or  $Cu_2O$  loading, ranging from 2%wt. to 6%wt., were prepared by impregnation method. The characterization results of studied catalysts can be concluded that:

- Addition of  $Ag_2O$  and  $Cu_2O$  over  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst increases rutile phase of  $TiO_2$  support.
- Addition of  $Ag_2O$  slightly decreases specific surface area and total acid sites of the catalyst.
- Addition of  $Cu_2O$  slightly decreases specific surface area of the catalyst, whereas total acid sites of the catalyst increases with enhancement of  $Cu_2O$  loading.

The activity of  $Ag_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$  and  $Cu_2O$ -doped  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts on  $NH_3$ -SCR reaction can be concluded that:

- $Ag_2O$  doping on  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst shows negative effect to  $NH_3$ -SCR reaction.

- $\text{Cu}_2\text{O}$  doping on  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst influences the different catalyst performance in two temperature regions. With lower  $\text{Cu}_2\text{O}$  loading, catalytic activity increases at high temperature, while higher  $\text{Cu}_2\text{O}$  loading catalytic activity enhances at low temperature.

## 5.2 Recommendations

For the further study of  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts for  $\text{NH}_3\text{-SCR}$  reaction.

- Variation of  $\text{Ag}_2\text{O}$  or  $\text{Cu}_2\text{O}$  loading must be regarded to find optimization configuration.
- Influence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  on  $\text{DeNO}_x$ -activity should be considered.
- Investigation in other species during  $\text{NH}_3\text{-SCR}$  reaction must be identified to analyze side reactions and to determine selectivity of reaction.
- In term of industry, studied catalysts must be investigated by monolithic type instead of powder form.
- Chemisorption technique should be investigated in further for dispersion of active sites study.
- FTIR-pyridine adsorption should be investigated in further for Lewis and Brønsted acid site study.

## REFERENCES

- [1] Roy, S., Hegde, M.S., and Madras, G. Catalysis for NO<sub>x</sub> abatement. Applied Energy 86(11) (2009): 2283-2297.
- [2] Chang, X., Lu, G., Guo, Y., Wang, Y., and Guo, Y. A high effective adsorbent of NO<sub>x</sub>: Preparation, characterization and performance of Ca-beta zeolites. Microporous and Mesoporous Materials 165 (2013): 113-120.
- [3] Vargas, M.A.L., Casanova, M., Trovarelli, A., and Busca, G. An IR study of thermally stable V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> SCR catalysts modified with silica and rare-earths (Ce, Tb, Er). Applied Catalysis B: Environmental 75(3-4) (2007): 303-311.
- [4] Zhang, R., Yang, W., Luo, N., Li, P., Lei, Z., and Chen, B. Low-temperature NH<sub>3</sub>-SCR of NO by lanthanum manganite perovskites: Effect of A-/B-site substitution and TiO<sub>2</sub>/CeO<sub>2</sub> support. Applied Catalysis B: Environmental 146 (2014): 94-104.
- [5] Schwämmle, T., Bertsche, F., Hartung, A., Brandenstein, J., Heidel, B., and Scheffknecht, G. Influence of geometrical parameters of honeycomb commercial SCR-DeNO<sub>x</sub>-catalysts on DeNO<sub>x</sub>-activity, mercury oxidation and SO<sub>2</sub>/SO<sub>3</sub>-conversion. Chemical Engineering Journal 222 (2013): 274-281.
- [6] Schuricht, F. and Reschetilowski, W. Simultaneous selective catalytic reduction (SCR) of NO<sub>x</sub> and N<sub>2</sub>O over Ag/ZSM-5 – Catalytic studies and mechanistic implications. Microporous and Mesoporous Materials 164 (2012): 135-144.
- [7] H. Hamada, Y.K., M. Sasaki, T. Ito. Applied Catalysis 64 (1990).
- [8] H.C. Yao, M.S., in: R.L. Klemesh, J.G. Larson (Eds.). The Catalytic Chemistry of Nitrogen Oxides. 1975, Plenum Press: New York. 45.
- [9] S. Sato, H.H., H. Yahiro, N. Mizuno, M. Ywamoto. Catalysis Letters 12 (1992): 193.
- [10] Si, Z., Weng, D., Wu, X., Li, J., and Li, G. Structure, acidity and activity of CuO<sub>x</sub>/WO<sub>x</sub>-ZrO<sub>2</sub> catalyst for selective catalytic reduction of NO by NH<sub>3</sub>. Journal of Catalysis 271(1) (2010): 43-51.



- [11] Nedyalkova, R., Kamasamudram, K., Currier, N.W., Li, J., Yezerets, A., and Olsson, L. Experimental evidence of the mechanism behind NH<sub>3</sub> overconsumption during SCR over Fe-zeolites. Journal of Catalysis 299 (2013): 101-108.
- [12] Wan, Y., et al. Ni-Mn bi-metal oxide catalysts for the low temperature SCR removal of NO with NH<sub>3</sub>. Applied Catalysis B: Environmental 148-149 (2014): 114-122.
- [13] Busca, G., Lietti, L., Ramis, G., and Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO<sub>x</sub> by ammonia over oxide catalysts: A review. Applied Catalysis B: Environmental 18(1-2) (1998): 1-36.
- [14] I.E. Wachs, R.Y.S., S.S. Chan and C. Chersich. Chemtech (1985): 756.
- [15] J. Svachula, L.J.A., N. Ferlazzo, P. Forzatti, E. Tronconi and F. Bregani. Industrial & Engineering Chemistry Research 32 (1993): 826.
- [16] V. Nikolov, D.K.a.A.A. Catalysis Reviews: Science and Engineering 33 (1991): 319.
- [17] A. Kato, S.M., F. Nakajima, M. Imanari and Y. Watanabe. The Journal of Physical Chemistry 85 (1981): 1710.
- [18] G. Ramis, Y.L., G. Busca, M. Turco, E. Kotur and R.J. Willey. Journal of Catalysis 157 (1995): 523.
- [19] G.L. Bauerle, S.C.W.a.K.N. Industrial and Engineering Chemistry Product Research and Development 14 (1975): 268.
- [20] R.J. Willey, J.W.E.a.J.R.K. Industrial and Engineering Chemistry Product Research and Development 24 (1985): 226.
- [21] Westermann, A., Azambre, B., and Koch, A. Effect of Ag, Pd and Co promoters on the Selective Catalytic Reduction (SCR) of NO<sub>x</sub> by ethanol over sulfated ceria-zirconia catalysts. Catalysis Today 191(1) (2012): 65-74.
- [22] Tamm, S., Fogel, S., Gabrielsson, P., Skoglundh, M., and Olsson, L. The effect of the gas composition on hydrogen-assisted NH<sub>3</sub>-SCR over Ag/Al<sub>2</sub>O<sub>3</sub>. Applied Catalysis B: Environmental 136-137 (2013): 168-176.

- [23] Flura, A., Can, F., Courtois, X., Royer, S., and Duprez, D. High-surface-area zinc aluminate supported silver catalysts for low-temperature SCR of NO with ethanol. Applied Catalysis B: Environmental 126 (2012): 275-289.
- [24] Shimizu, K.-i. and Satsuma, A. Hydrogen assisted urea-SCR and NH<sub>3</sub>-SCR with silver–alumina as highly active and SO<sub>2</sub>-tolerant de-NO<sub>x</sub> catalysis. Applied Catalysis B: Environmental 77(1-2) (2007): 202-205.
- [25] Kondratenko, V.A., Bentrup, U., Richter, M., Hansen, T.W., and Kondratenko, E.V. Mechanistic aspects of N<sub>2</sub>O and N<sub>2</sub> formation in NO reduction by NH<sub>3</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>: The effect of O<sub>2</sub> and H<sub>2</sub>. Applied Catalysis B: Environmental 84(3-4) (2008): 497-504.
- [26] Männikkö, M., Skoglundh, M., and Ingelsten, H.H. Selective catalytic reduction of NO<sub>x</sub> with methanol over supported silver catalysts. Applied Catalysis B: Environmental 119-120 (2012): 256-266.
- [27] Rao, K.N. and Ha, H.P. SO<sub>2</sub> promoted alkali metal doped Ag/Al<sub>2</sub>O<sub>3</sub> catalysts for CH<sub>4</sub>-SCR of NO<sub>x</sub>. Applied Catalysis A: General 433-434 (2012): 162-169.
- [28] Fogel, S., Doronkin, D.E., Gabrielsson, P., and Dahl, S. Optimisation of Ag loading and alumina characteristics to give sulphur-tolerant Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub>-assisted NH<sub>3</sub>-SCR of NO<sub>x</sub>. Applied Catalysis B: Environmental 125 (2012): 457-464.
- [29] Thirupathi, B. and Smirniotis, P.G. Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO<sub>2</sub> catalyst and its effect on the selective reduction of NO with NH<sub>3</sub> at low-temperatures. Applied Catalysis B: Environmental 110 (2011): 195-206.
- [30] Liu, H., Yu, X., and Yang, H. The integrated photocatalytic removal of SO<sub>2</sub> and NO using Cu doped titanium dioxide supported by multi-walled carbon nanotubes. Chemical Engineering Journal 243(0) (2014): 465-472.

- [31] Jiang, B., Liu, Y., and Wu, Z. Low-temperature selective catalytic reduction of NO on MnO(x)/TiO(2) prepared by different methods. J Hazard Mater 162(2-3) (2009): 1249-54.
- [32] Yu, W., Wu, X., Si, Z., and Weng, D. Influences of impregnation procedure on the SCR activity and alkali resistance of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst. Applied Surface Science 283 (2013): 209-214.
- [33] Wu, Z., Jiang, B., Liu, Y., Zhao, W., and Guan, B. Experimental study on a low-temperature SCR catalyst based on MnO(x)/TiO(2) prepared by sol-gel method. J Hazard Mater 145(3) (2007): 488-94.
- [34] Debecker, D.P., Hulea, V., and Mutin, P.H. Mesoporous mixed oxide catalysts via non-hydrolytic sol-gel: A review. Applied Catalysis A: General 451 (2013): 192-206.
- [35] Hegedus, J.W.B.a.L.L. Industrial & Engineering Chemistry Research 30 (1991): 969.
- [36] Hosten, L.J.P.a.L.H. Catalysis Today 17 (1993): 151.
- [37] I. Nam, J.W.E.a.I.R.K. Industrial and Engineering Chemistry Product Research and Development 25 (1986): 1186.
- [38] Marangozis, J. Industrial & Engineering Chemistry Research 31 (1992): 987.
- [39] Nobe, W.C.W.a.K. Industrial and Engineering Chemistry Product Research and Development 23 (1984): 564.
- [40] S.N. Orlik, V.A.O.a.M.G.M.-K. Kinetics and Catalysis (Kinetika i Kataliz) 36 (1995): 284.
- [41] Inomata, M., Miyamoto, A., and Murakami, Y. Mechanism of the reaction of NO and NH<sub>3</sub> on vanadium oxide catalyst in the presence of oxygen under the dilute gas condition. Journal of Catalysis 62(1) (1980): 140-148.
- [42] L. Lietti, P.F.a.F.B. Industrial & Engineering Chemistry Research 35 (1996): 3884.
- [43] Kerkhof, F.J.J.G.J.a.F.M.G.v.d. KEMA Scientific & Technological Report 3 (1985): 71.

- [44] M. deBoer, A.J.v., D.C. Koningsberger, F.J.J.G. Janssen, T. Koerts, J.W. Geus. New Developments in Selective Oxidations by Heterogeneous Catalysis, ed. P. Ruiz, B.D. Amsterdam: Elsevier, 1992.
- [45] M. de Boer, H.H., R.J.M. Mos, R.G. Leliveld, A.J.van Dillen and J.W. Geus. Catalysis Today 17 (1993): 189.
- [46] W.B. Williamson, D.R.F.a.J.H.L. Journal of Catalysis 37 (1975): 258.
- [47] L. Lietti, P.F., G. Ramis, G. Busca, F. Bregani. Applied Catalysis B 3 (1993): 13.
- [48] V. Nikolov, D.K., A. Anastasov. Catalysis Reviews: Science and Engineering 33 (1991): 319.
- [49] L. Lietti, J.L.A., P. Forzatti, G. Busca, G. Ramis, E. and Giamello, F.B. Catalysis Today 29 (1996): 143.
- [50] L. Lietti, J.S., P. Forzatti, G. Busca, G. Ramis, F. and Bregani. Catalysis Today 17 (1993): 131.
- [51] L.J. Alemany, F.B., G. Busca, G. Ramis, D. Robba, G.P. and Toledo, M.T. Applied Catalysis B 248 (1996): 299.
- [52] Ramis, G., Busca, G., Bregani, F., and Forzatti\*, P. Fourier transform-infrared study of the adsorption and coadsorption of nitric oxide, nitrogen dioxide and ammonia on vanadia-titania and mechanism of selective catalytic reduction. Applied Catalysis 64(0) (1990): 259-278.
- [53] T.Z. Srnak, J.A.D., B.S. Clausen, E. Tornquist, N.-Y. and Topsøe. Journal of Catalysis 135 (1991): 246.
- [54] G. Ramis, G. and Busca, V.L., P. Forzatti. Applied Catalysis 64 (1990): 243.
- [55] G. Busca, H.S., O. Saur, J.C. Lavalley, V. and Lorenzelli. Applied Catalysis 14 (1985): 245.
- [56] M.C. Kung, H.H.K. Catalysis Reviews: Science and Engineering 27 (1985): 425.
- [57] J.A. Odriozola, H.H., G.A. Somorjai, J.F. Garcia and de la Banda, P.P. Journal of Catalysis 119 (1989): 71.

- [58] G. Centi, S.P., P. Biglino, E. Giamello. Journal of Catalysis 152 (1995): 75.
- [59] A.W. Aylor, S.C.L., A.T. Bell, J.A. Reimer. Journal of Catalysis 157 (1995): 592.
- [60] K. Hadjiivanov, D.K., G. Ramis, G. Busca. Applied Catalysis B 7 (1996): 251.
- [61] G. Centi, S.P. Applied Catalysis A 132 (1995): 179.
- [62] N.Y. Topsøe, H.T., J.H. Dumesic. Adsorption, Activation, and Oxidation of Ammonia over SCR Catalysts. Journal of Catalysis 151 (1995): 226,241.
- [63] Tronconi, E., Lietti, L., Forzatti, P., and Malloggi, S. Experimental and theoretical investigation of the dynamics of the SCR - DeNO<sub>x</sub> reaction. Chemical Engineering Science 51(11) (1996): 2965-2970.
- [64] Lietti, L., et al. Chemical, structural and mechanistic aspects on NO<sub>x</sub> SCR over commercial and model oxide catalysts. Catalysis Today 42(1-2) (1998): 101-116.
- [65] Ozkan, U.S., Cai, Y.P., and Kumthekar, M.W. Investigation of the Mechanism of Ammonia Oxidation and Oxygen Exchange over Vanadia Catalysts Using N-15 and O-18 Tracer Studies. Journal of Catalysis 149(2) (1994): 375-389.
- [66] Ozkan, U.S., Cai, Y.P., and Kumthekar, M.W. Investigation of the Reaction Pathways in Selective Catalytic Reduction of NO with NH<sub>3</sub> over V<sub>2</sub>O<sub>5</sub> Catalysts: Isotopic Labeling Studies Using <sup>18</sup>O<sub>2</sub>, <sup>15</sup>NH<sub>3</sub>, <sup>15</sup>NO, and <sup>15</sup>N<sup>18</sup>O. Journal of Catalysis 149(2) (1994): 390-403.
- [67] Janssen, F.J.J.G., Van den Kerkhof, F.M.G., Bosch, H., and Ross, J.R.H. Mechanism of the reaction of nitric oxide, ammonia, and oxygen over vanadia catalysts. 2. Isotopic transient studies with oxygen-18 and nitrogen-15. The Journal of Physical Chemistry 91(27) (1987): 6633-6638.
- [68] Janssen, F.J.J.G., Van den Kerkhof, F.M.G., Bosch, H., and Ross, J.R.H. Mechanism of the reaction of nitric oxide, ammonia, and oxygen over vanadia catalysts. I. The role of oxygen studied by way of isotopic transients under dilute conditions. The Journal of Physical Chemistry 91(23) (1987): 5921-5927.

- [69] Winter, E.R.S. The catalytic decomposition of nitric oxide by metallic oxides. Journal of Catalysis 22(2) (1971): 158-170.
- [70] Centi, G., Perathoner, S., Biglino, D., and Giamello, E. Adsorption and Reactivity of No on Copper-on-Alumina Catalysts: I. Formation of Nitrate Species and Their Influence on Reactivity in No and NH<sub>3</sub> Conversion. Journal of Catalysis 152(1) (1995): 75-92.
- [71] Centi, G. and Perathoner, S. Adsorption and Reactivity of No on Copper-on-Alumina Catalysts: II. Adsorbed Species and Competitive Pathways in the Reaction of No with NH<sub>3</sub> and O<sub>2</sub>. Journal of Catalysis 152(1) (1995): 93-102.
- [72] Busca, G., Larrubia, M.A., Arrighi, L., and Ramis, G. Catalytic abatement of NO<sub>x</sub>: Chemical and mechanistic aspects. Catalysis Today 107-108 (2005): 139-148.
- [73] Kapteijn, F., Singoredjo, L., Dekker, N.J.J., and Moulijn, J.A. Kinetics of the selective catalytic reduction of nitrogen oxide (NO) with ammonia over manganese oxide (Mn<sub>2</sub>O<sub>3</sub>)-tungsten oxide (WO<sub>3</sub>)/gamma.-alumina. Industrial & Engineering Chemistry Research 32(3) (1993): 445-452.
- [74] Kapteijn, F., et al. Alumina-Supported Manganese Oxide Catalysts: II. Surface Characterization and Adsorption of Ammonia and Nitric Oxide. Journal of Catalysis 150(1) (1994): 105-116.
- [75] Komatsu, T., Nunokawa, M., Moon, I.S., Takahara, T., Namba, S., and Yashima, T. Kinetic Studies of Reduction of Nitric Oxide with Ammonia on Cu<sup>2+</sup>-Exchanged Zeolites. Journal of Catalysis 148(2) (1994): 427-437.
- [76] Ingemar Odenbrand, C.U., T. Lundin, S., and A.H. Andersson, L. Catalytic reduction of nitrogen oxides 1. The reduction of NO. Applied Catalysis 18(2) (1985): 335-352.
- [77] Gasior, M., Haber, J., Machej, T., and Czeppe, T. Mechanism of the reaction NO + NH<sub>3</sub> ON V<sub>2</sub>O<sub>5</sub> catalysts. Journal of Molecular Catalysis 43(3) (1988): 359-369.

- [78] Leong, K.H., Monash, P., Ibrahim, S., and Saravanan, P. Solar photocatalytic activity of anatase TiO<sub>2</sub> nanocrystals synthesized by non-hydrolytic sol-gel method. Solar Energy 101 (2014): 321-332.
- [79] Eskandarloo, H., Badiei, A., Behnajady, M.A., and Ziarani, G.M. UV-LEDs assisted preparation of silver deposited TiO<sub>2</sub> catalyst bed inside microchannels as a high efficiency microphotoreactor for cleaning polluted water. Chemical Engineering Journal 270 (2015): 158-167.
- [80] Zhang, S. and Zhong, Q. Surface characterization studies on the interaction of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst for low temperature SCR of NO with NH<sub>3</sub>. Journal of Solid State Chemistry 221 (2015): 49-56.
- [81] Altomare, M., Dozzi, M.V., Chiarello, G.L., Di Paola, A., Palmisano, L., and Selli, E. High activity of brookite TiO<sub>2</sub> nanoparticles in the photocatalytic abatement of ammonia in water. Catalysis Today 252 (2015): 184-189.
- [82] Zhang, S., Yang, X., and Zhong, Q. Cluster molecular modeling of strong interaction for F-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> supported catalyst. Journal of Fluorine Chemistry 153 (2013): 26-32.
- [83] Kim, Y.J., et al. High deNO<sub>x</sub> performance of Mn/TiO<sub>2</sub> catalyst by NH<sub>3</sub>. Catalysis Today 151(3-4) (2010): 244-250.
- [84] Ma, Z., Weng, D., Wu, X., and Si, Z. Effects of WO<sub>x</sub> modification on the activity, adsorption and redox properties of CeO<sub>2</sub> catalyst for NO<sub>x</sub> reduction with ammonia. Journal of Environmental Sciences 24(7) (2012): 1305-1316.
- [85] Yu, L., Yang, X., Ye, Y., Peng, X., and Wang, D. Silver nanoparticles decorated anatase TiO<sub>2</sub> nanotubes for removal of pentachlorophenol from water. J Colloid Interface Sci 453 (2015): 100-6.
- [86] Aysin, B., Ozturk, A., and Park, J. Silver-loaded TiO<sub>2</sub> powders prepared through mechanical ball milling. Ceramics International 39(6) (2013): 7119-7126.

- [87] Wu, Z., Jiang, B., and Liu, Y. Effect of transition metals addition on the catalyst of manganese/titania for low-temperature selective catalytic reduction of nitric oxide with ammonia. Applied Catalysis B: Environmental 79(4) (2008): 347-355.
- [88] Wang, D., Zhang, L., Li, J., Kamasamudram, K., and Epling, W.S. NH<sub>3</sub>-SCR over Cu/SAPO-34 – Zeolite acidity and Cu structure changes as a function of Cu loading. Catalysis Today 231 (2014): 64-74.
- [89] Chen, L., Li, J., and Ge, M. The poisoning effect of alkali metals doping over nano V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts on selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>. Chemical Engineering Journal 170(2-3) (2011): 531-537.
- [90] Satsuma, A., et al. Preparation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst for NH<sub>3</sub>-SCR: Controlling factor of TiO<sub>2</sub> support for highly active catalyst. in E.M. Gaigneaux, M.D.D.E.D.V.S.H.P.A.J.J.A.M. and Ruiz, P. (eds.), Studies in Surface Science and Catalysis, pp. 785-792: Elsevier, 2006.





APPENDICES

จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY

## APPENDIX A

### ESTIMATION OF CATALYST PREPARATION

#### Preparation of $V_2O_5$ - $WO_3$ / $TiO_2$ catalyst

Reagents:

$TiO_2$  powder was prepared by a sol-gel method.

Ammonium metavanadate 99.999%,  $NH_4VO_3$  (Aldrich Chemical)

Ammonium metatungstate hydrate 99.99%,  $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$  (Aldrich Chemical)

Oxalic acid hydrate (Fluka)

Calculation for preparation of  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst

To determine the catalyst composition

Basis: 1 g of catalyst

$$V_2O_5 = 0.03 \times 1 = 0.03 \text{ g}$$

$$WO_3 = 0.07 \times 1 = 0.07 \text{ g}$$

$$\therefore TiO_2 = 1 - 0.07 - 0.03 = 0.90 \text{ g}$$

$V_2O_5$  0.03 g was prepared from  $NH_4VO_3$  as precursor of vanadium

$$\begin{aligned} NH_4VO_3 \text{ used} &= \frac{V_2O_5 \text{ required}}{MW \text{ of } V_2O_5} \times MW \text{ of } NH_4VO_3 \\ &= 2 \times \frac{0.03 \text{ g}}{181.88 \frac{\text{g}}{\text{mol}}} \times 116.98 \frac{\text{g}}{\text{mol}} \\ &= 0.0386 \text{ g} \end{aligned}$$

Note: Molecular weight of  $NH_4VO_3$  equal to 116.98 g/mole

Molecular weight of  $V_2O_5$  equal to 181.88 g/mole

To dissolve  $\text{NH}_4\text{VO}_3$ , oxalic acid required with molar ratio of  $\text{NH}_4\text{VO}_3$ /oxalic acid equal 1:1

$$\begin{aligned}\text{Oxalic acid used} &= \frac{0.0386 \text{ g}}{116.98 \text{ g/mol}} \times 126.07 \text{ g/mol} \\ &= 0.0416 \text{ g}\end{aligned}$$

Note: Molecular weight of oxalic acid equal to 126.07 g/mole

$\text{WO}_3$  0.07 g was prepared from  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  as precursor of tungsten

$$\begin{aligned}(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O} \text{ used} &= \frac{\text{WO}_3 \text{ required}}{\text{MW of WO}_3} \times \text{MW of } (\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O} \\ &= \frac{\text{WO}_3 \text{ required}}{\text{MW of WO}_3} \times \text{MW of WCl}_6 \\ &= \frac{0.07 \text{ g}}{12 \times 231.84 \text{ g/mol}} \times 2956.3 \text{ g/mol} \frac{0.35 \text{ g}}{231.84 \text{ g/mol}} \times 396.56 \text{ g/mol} \\ &= 0.0743 \text{ g}\end{aligned}$$

Note: Molecular weight of  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$  equal to 2956.3 g/mole

Molecular weight of  $\text{WO}_3$  equal to 231.84 g/mole

### Preparation of Ag<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts

Reagents:

TiO<sub>2</sub> powder was prepared by a sol-gel method.

Ammonium metavanadate 99.999%, NH<sub>4</sub>VO<sub>3</sub> (Aldrich Chemical)

Ammonium metatungstate hydrate 99.99%, (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O (Aldrich Chemical)

Oxalic acid hydrate (Fluka)

Silver nitrate >99.999%, AgNO<sub>3</sub> (Aldrich Chemical)

Calculation for preparation of Ag<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts

To determine the catalyst composition (for example, 3V7W2Ag)

Basis: 1 g of catalyst

$$\text{Ag}_2\text{O} = 0.02 \times 1 = 0.02 \text{ g}$$

$$\text{V}_2\text{O}_5 = 0.03 \times 1 = 0.03 \text{ g}$$

$$\text{WO}_3 = 0.07 \times 1 = 0.07 \text{ g}$$

$$\therefore \text{TiO}_2 = 1 - 0.07 - 0.03 - 0.02 = 0.88 \text{ g}$$

Ag<sub>2</sub>O 0.02 g was prepared from AgNO<sub>3</sub> as precursor of silver

$$\begin{aligned} \text{AgNO}_3 \text{ used} &= \frac{\text{Ag}_2\text{O required}}{\text{MW of Ag}_2\text{O}} \times \text{MW of AgNO}_3 \\ &= 2 \times \frac{0.02 \text{ g}}{231.74 \text{ g/mol}} \times 169.87 \text{ g/mol} \\ &= 0.0293 \text{ g} \end{aligned}$$

Note: Molecular weight of AgNO<sub>3</sub> equal to 169.87 g/mole

Molecular weight of Ag<sub>2</sub>O equal to 231.74 g/mole

Calculation of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> was mentioned above.

### Preparation of Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts

Reagents:

TiO<sub>2</sub> powder was prepared by a sol-gel method.

Ammonium metavanadate 99.999%, NH<sub>4</sub>VO<sub>3</sub> (Aldrich Chemical)

Ammonium metatungstate hydrate 99.99%, (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O (Aldrich Chemical)

Oxalic acid hydrate (Fluka)

Copper nitrate >99.99%, Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O (Aldrich Chemical)

Calculation for preparation of Cu<sub>2</sub>O-doped V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts

To determine the catalyst composition (for example, 3V7W6Cu)

Basis: 1 g of catalyst

$$\text{Cu}_2\text{O} = 0.06 \times 1 = 0.06 \text{ g}$$

$$\text{V}_2\text{O}_5 = 0.03 \times 1 = 0.03 \text{ g}$$

$$\text{WO}_3 = 0.07 \times 1 = 0.07 \text{ g}$$

$$\therefore \text{TiO}_2 = 1 - 0.07 - 0.03 - 0.06 = 0.84 \text{ g}$$

Cu<sub>2</sub>O 0.06 g was prepared from Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O as precursor of copper

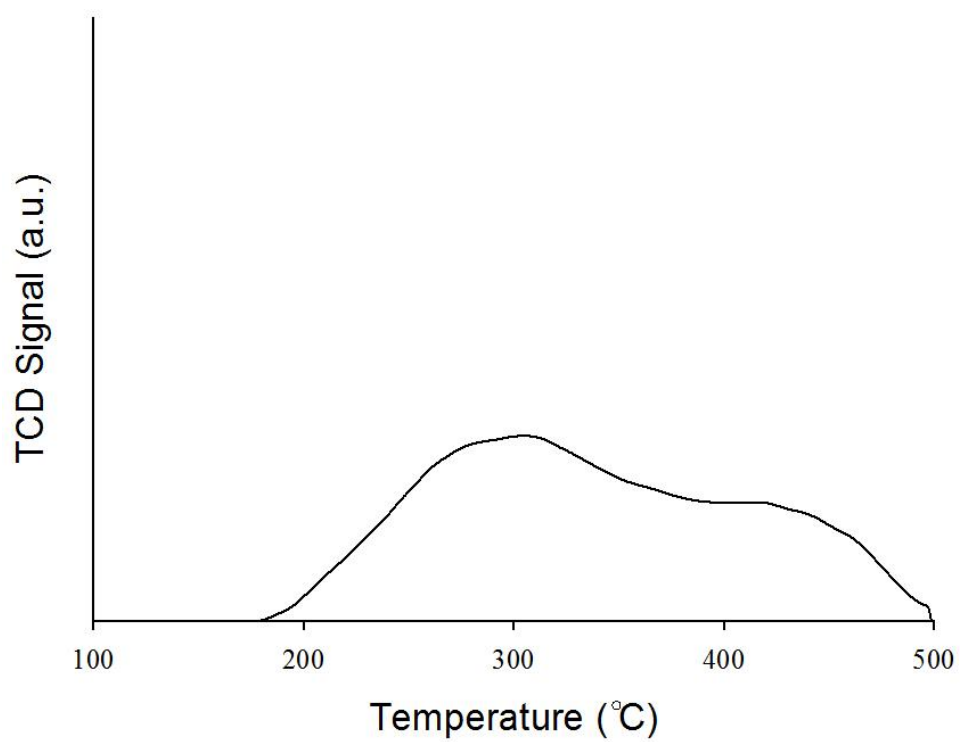
$$\begin{aligned} \text{Cu(NO}_3)_2 \cdot 2.5\text{H}_2\text{O used} &= \frac{\text{Cu}_2\text{O required}}{\text{MW of Cu}_2\text{O}} \times \text{MW of Cu(NO}_3)_2 \cdot 2.5\text{H}_2\text{O} \\ &= 2 \times \frac{0.06 \text{ g}}{143.09 \text{ g/mol}} \times 232.59 \text{ g/mol} \\ &= 0.1951 \text{ g} \end{aligned}$$

Note: Molecular weight of Cu(NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O equal to 232.59 g/mole

Molecular weight of Cu<sub>2</sub>O equal to 143.09 g/mole

Calculation of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> was mentioned above.

## APPENDIX B

TEMPERATURE PROGRAMMED DESORPTION PROFILE (NH<sub>3</sub>-TPD)Figure B.1 NH<sub>3</sub>-TPD profile of 3V7W catalyst

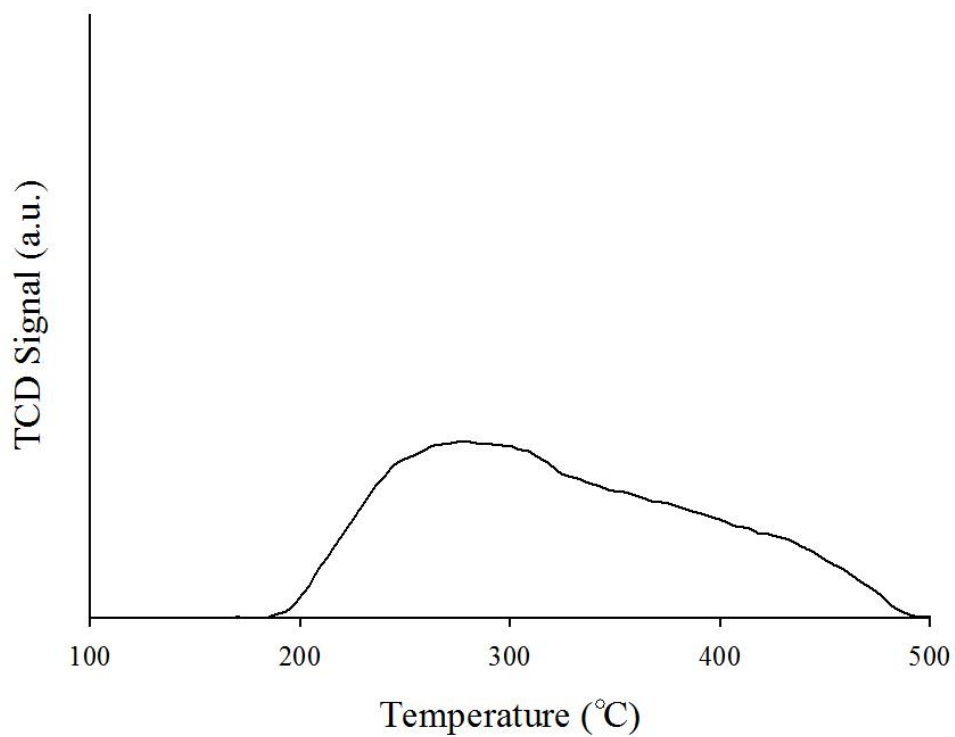


Figure B.2 NH<sub>3</sub>-TPD profile of 3V7W2Ag catalyst

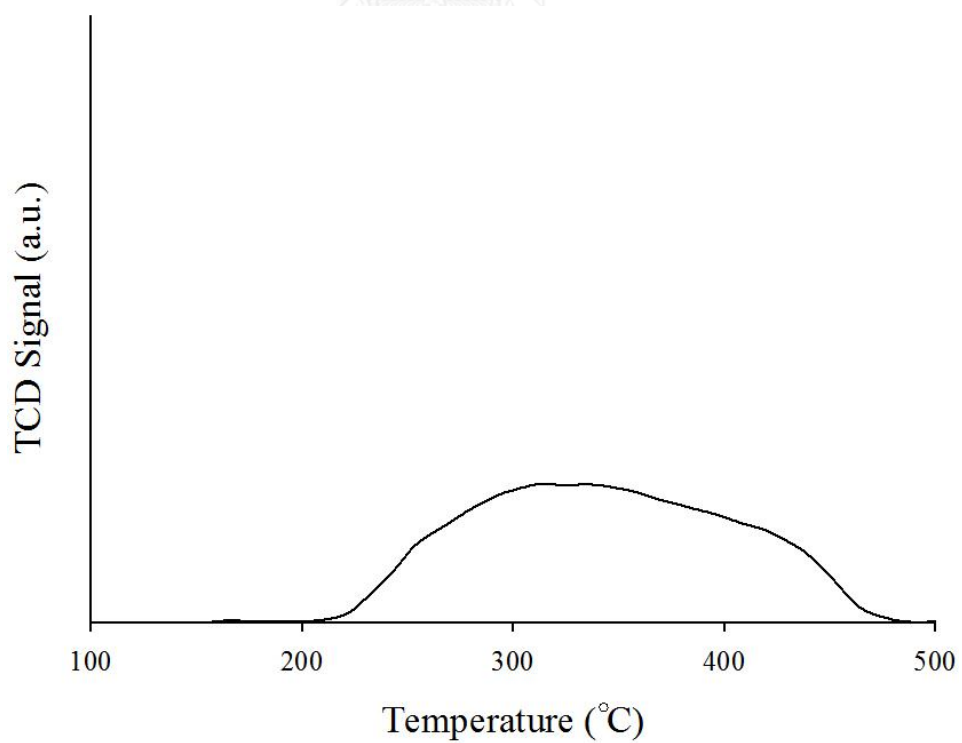


Figure B.3 NH<sub>3</sub>-TPD profile of 3V7W4Ag catalyst

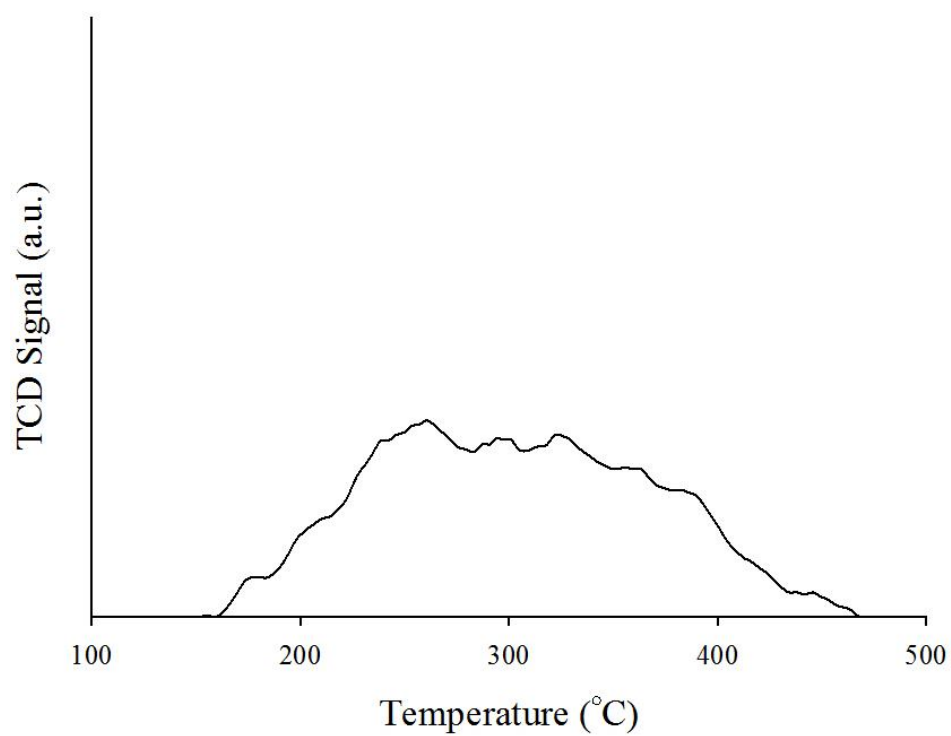


Figure B.4 NH<sub>3</sub>-TPD profile of 3V7W6Ag catalyst

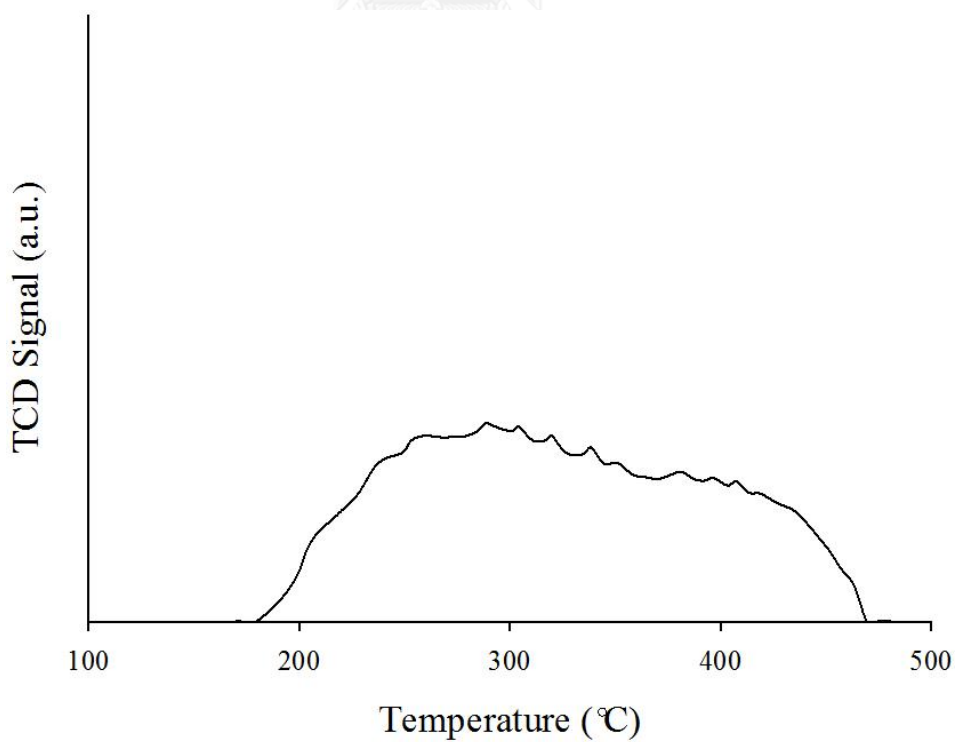


Figure B.5 NH<sub>3</sub>-TPD profile of 3V7W2Cu catalyst



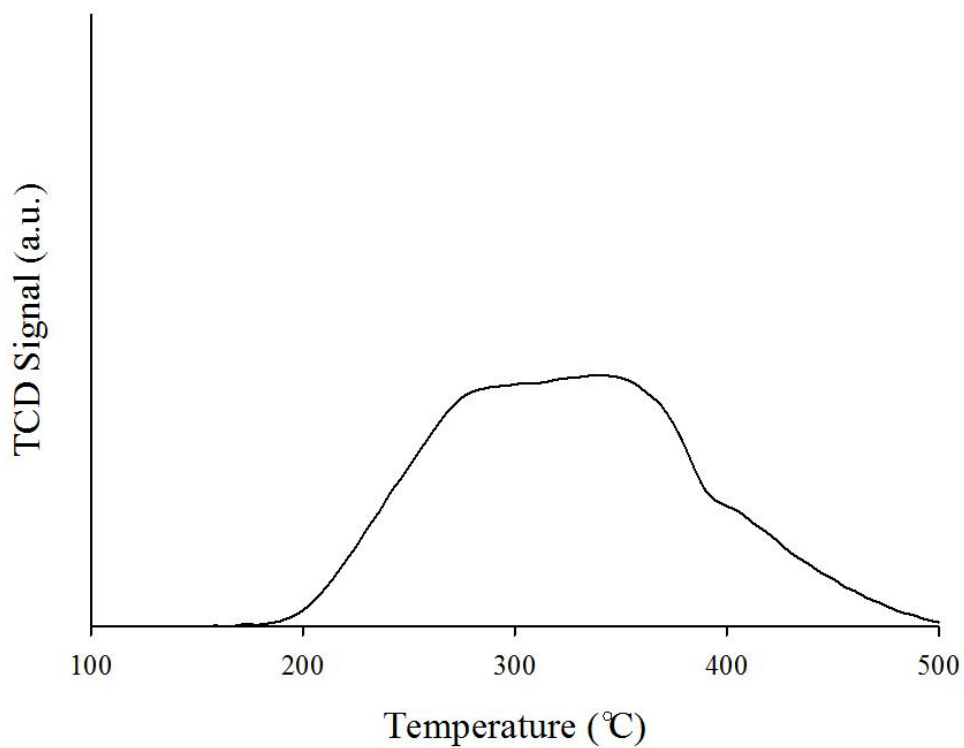


Figure B.6 NH<sub>3</sub>-TPD profile of 3V7W4Cu catalyst

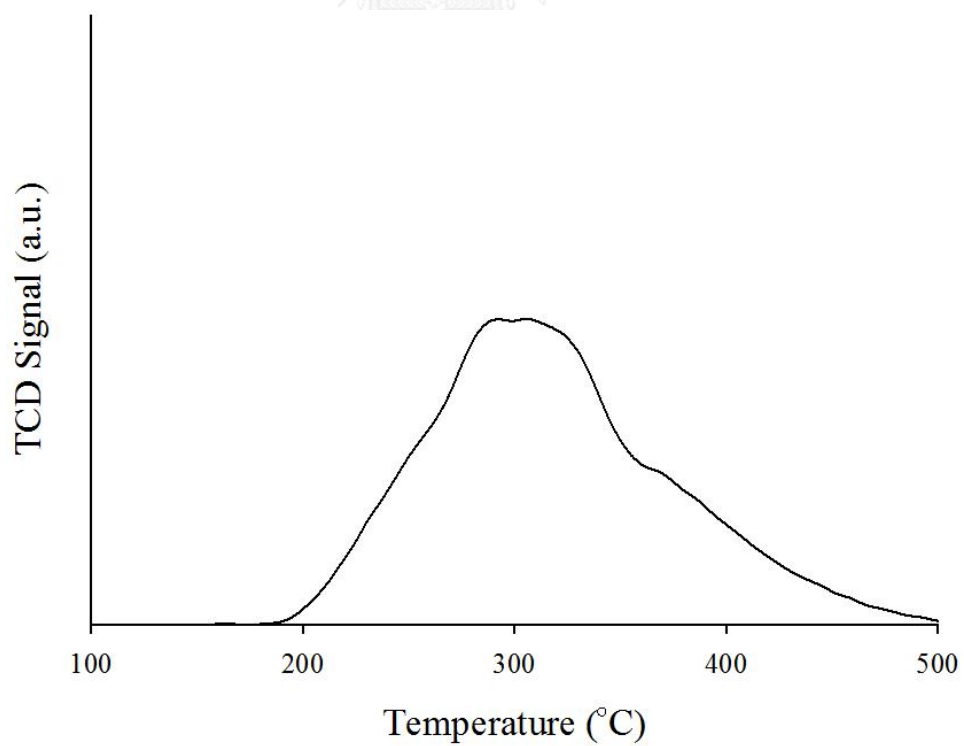


Figure B.7 NH<sub>3</sub>-TPD profile of 3V7W6Cu catalyst

## APPENDIX C

### CALCULATION OF TOTAL ACID SITES

The measurement is based on the NH<sub>3</sub>-TPD result. Peak areas are used for quantitative calculation. Total acid sites was estimated by total area under peak, presented in Table C.1.

**Table C.1** Total area under peak of studied catalysts

Sample	Peak area
3V7W	5.884
3V7W2Ag	5.265
3V7W4Ag	4.229
3V7W6Ag	4.092
3V7W2Cu	6.600
3V7W4Cu	5.595
3V7W6Cu	6.589

For instance, total acid sites of 3V7W catalyst was calculated by this following step.

1. Commuting of peak area to peak volume

The volume of NH<sub>3</sub> was determined by equation  $y = 35.847x$ , which calibrated as show in Figure C.1.

$$\begin{aligned}
 \text{The volume of NH}_3 &= 35.847 \times \text{area} \\
 &= 35.847 \times 5.884 \\
 &= 210.9344 \text{ ml}
 \end{aligned}$$

2. Calculation for adsorbed volume of 15 %vol. of NH<sub>3</sub> in helium gas.

$$\begin{aligned}\text{Adsorbed volume} &= 0.15 \times \text{total peak volume} \\ &= 0.15 \times 210.9344 \text{ ml} \\ &= 31.6402 \text{ ml}\end{aligned}$$

3. Estimation of the total acid sites.

The amount of 0.1007 g of 3V7W catalyst was measured.

The total acid sites =

$$\begin{aligned}&\frac{\text{Adsorbed volume (mL)} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \text{ Pa} \cdot \text{mL} / \text{K} \cdot \mu\text{mol} \times 298 \text{ K} \times \text{weight of catalyst (g)}} \quad \frac{\text{Adsorbed volume (mL)} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{mL}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times \text{weight of catalyst (g)}} \\ &= \frac{31.6402 \text{ mL} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \text{ Pa} \cdot \text{mL} / \text{K} \cdot \mu\text{mol} \times 298 \text{ K} \times 0.1007 \text{ (g)}} \\ &= 12.8499 \text{ mmol/g}\end{aligned}$$

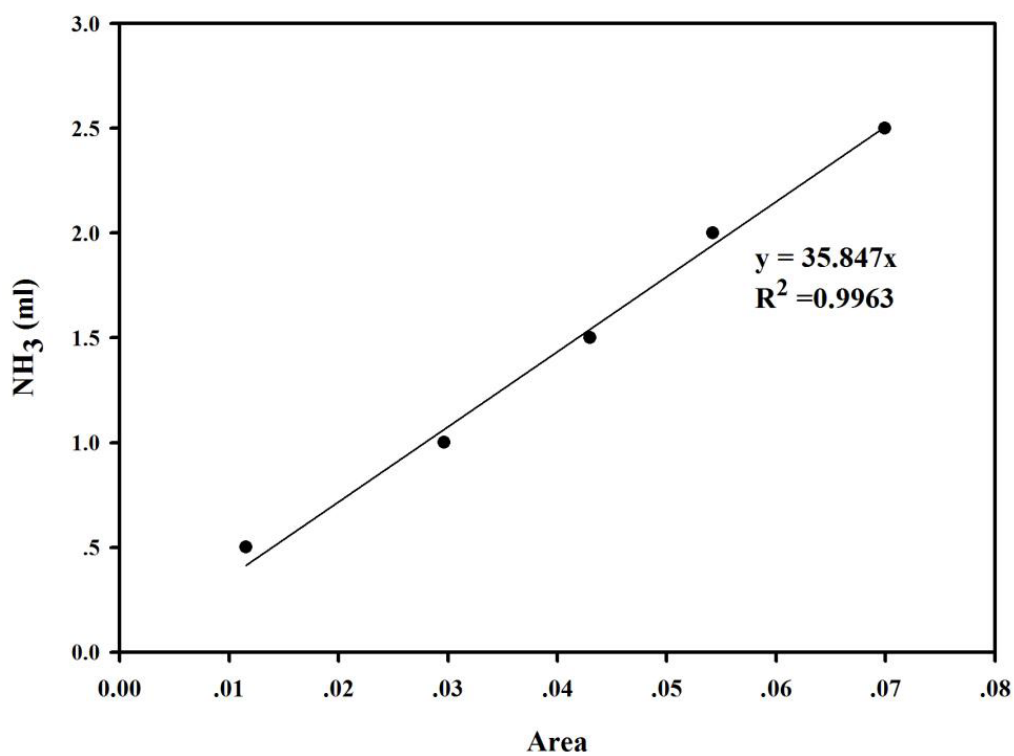


Figure C.1 Calibration curve of NH<sub>3</sub>

## APPENDIX D

## CALCULATION OF NO CONVERSION

Chromatogram results from GC were analyzed in order to determine the amount of NO in the outlet stream. For this example, 3V7W4Cu catalyst was used as a sample, and peak areas as a function of temperature present in Table D.1.

**Table D.1** Peak area of NO at each temperature for 3V7W4Cu catalyst

Temperature (°C)	Average peak area
Ambient	10,602
120	10165
150	9620
200	5482
250	2245
300	5128
350	7997
400	9649

Example calculation at 250°C

Assumption: SCR reaction does not occur at ambient temperature; therefore, it represents as in the feed stream containing with 120 ppm of NO.

The amount of NO at 250°C was calculated by interpolation method.

Peak area of NO was 10,602 implied to 120 ppm of NO.

$$\text{NO at 250}^\circ\text{C} = \frac{2245 \times 120 \text{ ppm}}{10,602} = 25.4 \text{ ppm}$$

From:  $\% \text{NO conversion} = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100$

Then  $\% \text{NO conversion} = \frac{120 - 25.4}{120} \times 100$

$\% \text{NO conversion} = 78.8$

Thus, NO conversion for 3V7W4Cu at 250°C was 79 %.

## APPENDIX E

## SETTING CONDITION OF SHIMADZU GC-2014

Shimadzu GC-2014 was applied to measure NO in the outlet stream. The detail of setting condition is described in Table E.1.

**Table E.1** Operating condition of Shimadzu GC-2014.

Shimadzu GC-2014	NO
Detector	ECD
Temperature Detector (°C)	200
Column	Hyasep-DB
Max temperature column (°C)	190
Temperature column (°C)	40
Inner Diameter column (mm)	0.1
Length column (m)	2
Temperature injector (°C)	-
Carrier gas	N <sub>2</sub>
Carrier gas flow	240 kPa
Add flow (kPa)	-
Sampling rate (msec)	80

## VITA

Mr. Natthakorn Jirathanasin was born on November 2, 1989 in Bangkok, Thailand. He finished high school from Saint Dominic School, Bangkok, and graduated the bachelor's degree of Science, Chemical Technology, Chulalongkorn University, in 2012. He continued his master's degree at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in May 2012.

### LIST OF PUBLICATIONS:

Natthakorn Jirathanasin and Akawat Sirisuk. EFFECT OF SILVER DOPING ON V2O5-WO3-TiO2 CATALYST FOR SELECTIVE CATALYTIC REDUCTION OF NOX BY AMMONIA AT LOW TEMPERATURE. Pure and Applied Chemistry International Conference 2014 (PACCON2014), Khon Kaen University, January 8-10, 2014.

