ปฏิกิริยารีดักชันโดยใช้ตัวเร่งปฏิกิริยาแบบเลือกเกิดของไนโตรเจนออกไซด์
โดยใช้แอมโมเนียบนตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่มี WO_3 และ MoO_3

นางสาวเกียรติลดา วารินศิริรักษ์

SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA OVER
V_2O_5/TiO_2 CONTAINING WO_3 AND MoO_3 CATALYSTS

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Thesis Title   SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA OVER V_2O_5/TiO_2 CONTAINING WO_3 AND MoO_3 CATALYSTS

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(Peangpit Wongmaneenil, D.Eng.)

เกียรติลดา วารินศิริรักษ์: ปฏิกิริยารีดักชันโดยใช้ตัวเร่งปฏิกิริยาแบบเลือกเกิดของไนโตรเจน ออกไซด์โดยใช้แอมโมเนียบนตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่มี WO_3 และ MoO_3. (SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA OVER V_2O_5/TiO_2 CONTAINING WO_3 AND MoO_3 CATALYSTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธราธร มงคลศรี, 83 หน้า.

งานวิจัยนี้ทำการศึกษาปฏิกิริยารีดักชันของก๊าซไนโตรเจนออกไซด์แบบเลือกเกิดด้วยก๊าซ แอมโมเนียบนตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่มี WO_3 และ MoO_3โดยเตรียมตัวรองรับ ไททาเนียมไดออกไซด์ด้วยวิธีโซล-เจล ทำการเติมโลหะวานาเดียม, ทังสเตนและโมลิบดินัมลงบน TiO_2ด้วยวิธีการเคลือบฝังเปียกแบบพอดีรูพรุน ทำการวิเคราะห์ตัวเร่งปฏิกิริยาโดยใช้เทคนิค ICP-OES, XRD, nitrogen adsorption, NH_3-TPD และ FT-IR การทดสอบตัวเร่งปฏิกิริยากระทำในช่วง อุณหภูมิ 100-450°C พบว่าตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่มี WO_3 และ MoO_3 เป็นตัวเร่งปฏิกิริยาที่ ทำงานได้ดีในช่วงอุณหภูมิต่ำถึงปานกลาง วิธีที่ดีที่สุดในการเตรียมตัวเร่งปฏิกิริยาคือ การเติม โลหะเป็นลำดับโดยเริ่มจากเติมโลหะ V แล้วเผาที่ 500 องศาเซลเซียส นาน 2 ชั่วโมง จากนั้นเติม โลหะ Mo แล้วเผาที่ 500 องศาเซลเซียส นาน 2 ชั่วโมง และเติมโลหะ W แล้วเผาที่ 500 องศา เซลเซียส นาน 2 ชั่วโมง นอกจากนี้ยังพบว่าการลดปริมาณของโลหะ W และ Mo ลงจากปริมาณ 7 และ 10 %โดยน้ำหนักตามลำดับนั้น ไม่ส่งผลดีต่อการเพิ่มประสิทธิภาพของปฏิกิริยาการกำจัดก๊าซ ไนโตรเจนออกไซด์ ดังนั้นปริมาณโลหะ V, W และ Mo บนตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่ เหมาะสมคือ 3, 7 และ 10 %โดยน้ำหนัก (คิดในรูปสารประกอบออกไซด์) ภายใต้สภาวะที่มีไอน้ำ และซัลเฟอร์ไดออกไซด์ ที่อุณหภูมิต่ำความว่องไวของตัวเร่งปฏิกิริยา V_2O_5/TiO_2 ที่มี WO_3 และ MoO_3 จะลดลง เนื่องจากซัลเฟอร์ไดออกไซด์และน้ำจะแย่งดูดซับลงบนตำแหน่งซึ่งสามารถดูดซับ แอมโมเนียได้ แต่ที่อุณหภูมิสูงนั้นซัลเฟอร์ไดออกไซด์และน้ำจะไปช่วยลดปฏิกิริยาแอมโมเนีย ออกซิเดชัน

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก	
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KIETLADA WARINSIRIRUX: SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDE BY AMMONIA OVER V_2O_5/TiO_2 CONTAINING WO_3 AND MoO_3 CATALYSTS. ADVISOR : ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 83 pp.

This work studies the selective catalytic reduction (SCR) of nitrogen oxide by ammonia over V_2O_5/TiO_2 containing WO_3 and MoO_3 catalysts. The support, titanium dioxide is prepared by a sol-gel method. The vanadium, tungsten and molybdenum are loaded to the prepared TiO_2 by incipient wetness method. Various techniques including ICP-OES, XRD, nitrogen adsorption, NH_3-TPD and FT-IR are employed to characterize the catalysts. The catalytic activity testing is carried out in a temperature range 100-450°C. The results indicate that 3VxWyMo catalyst system shows good catalytic performances at low to intermediate temperature. The sequence of loading metal oxides (V, W and Mo) and calcinations influences the SCR activity significantly. An optimal catalyst preparation is loading V, calcination at 500 °C for 2 hr, loading Mo, calcinations at 500 °C for 2 hr and finally loading W, calcinations at 500 °C for 2 hr. Moreover, the research also found that the decreasing of the contents of W and Mo down from 7 and 10 wt.% respectively does not improve the SCR activity. The suitable compositions of WO_3 and MoO_3 over V_2O_5/TiO_2 catalyst are 7 and 10 wt.% respectively. The presence of H_2O and SO_2 can reduce the oxidation of NH_3 to NO at high temperature. It is believed that H_2O and SO_2 can competitively adsorb with NH_3 on the site which can oxidize NH_3 to NO. The blocking of this site results in lower NH_3 oxidation.

Department : ____Chemical Engineer____   Student's Signature ....

Field of Study : ___Chemical Engineer___   Advisor's Signature ....

Academic Year :............2011............

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CHAPTER I

INTRODUCTION

1.1 Introduction

Nitrogen oxides (NO, NO_2 and N_2O) emission remains a major air pollutants in flue gas from both automobile and stationary sources. These undesirable byproducts have to be removed before emitting to the surroundings since they contribute to acid rain, photochemical smog, ozone depletion and green-house effects. In the past, many techniques have been developed continuously to reduce the emission of nitrogen oxides. Nitrogen oxides removal from waste gases from stationary sources can be achieved efficiently by using the so called selective catalytic reduction (SCR) process. This method has been developed continuously to reduce the emission of nitrogen oxides by ammonia. The SCR is the process that a reducing agent, NH_3 reacts selectively with the NO_x to produce nitrogen and water according to the two main reactions.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{(eq. 1.1)}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad \text{(eq. 1.2)}$$
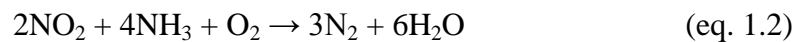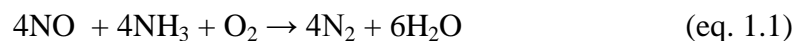
It is known that at the high temperature, the undesirable oxidation of NH_3 to form nitrogen oxides may also occur as side reactions. Ammonia reacts with oxygen rather than NO to form nitrogen oxides; NO, N_2O according to the reactions.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \text{(eq. 1.3)}$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad \text{(eq. 1.4)}$$

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \qquad \text{(eq. 1.5)}$$
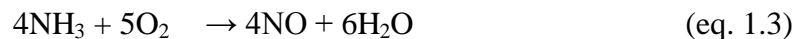
The commercial catalysts for SCR process are based on V_2O_5/TiO_2 mixed with WO_3 or MoO_3 using ammonia as a reducing agent. For the $V_2O_5\text{-}WO_3/TiO_2$, this reaction requires a higher temperature in the range of 300–400 ºC to obtain the desired removal efficiency of NO_x (Beretta et al, 1998 and Kaewbuddee, 2009) and

for the V_2O_5-MoO_3/TiO_2 requires a lower temperature in the range of 150–350 ºC for stationary source in order to minimize energy consumption (Taweesuk, 2011). For the reasons mentioned above, we are strongly interested in developing three mixed metal oxides (V_2O_5-WO_3-MoO_3) so as to develop and find the optimal catalyst for having wider operating temperature on the SCR reaction.

If sulfur dioxide presents in the combustion gases, it can be oxidized with O_2 to form sulfur trioxide via the oxidation reaction over V_2O_5 based catalyst. Sulfur trioxide ultimately reacts with ammonia or the catalyst and forms a sulfur compound, ammonium sulfates, which can foul catalyst and/or heat exchange surface, according to the reactions.

$$2SO_2 + O_2 \rightarrow 2SO_3 \quad\quad\quad\quad \text{(eq. 1.5)}$$
$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \quad\quad\quad\quad \text{(eq. 1.6)}$$
$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \quad\quad\quad\quad \text{(eq. 1.7)}$$
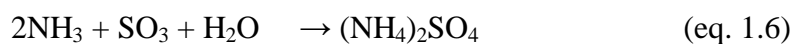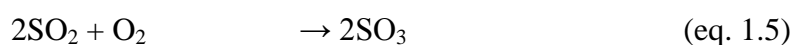
To avoid the oxidation of SO_2, the V_2O_5 content is kept low, being usually between 1-3% w/w. WO_3 or MoO_3 are employed in much larger amounts (nearby 10 and 6% w/w, respectively); it has been reported that they act both as "chemical" and "structural" promoters because they increase the reactivity of V_2O_5/TiO_2 catalysts and improve the mechanical, structural and morphological properties of the catalysts (Busca et al, 1998) and (Lietti et al, 2000).

Several studies have been published concerning the characterization and catalytic activity of V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 model and industrial SCR catalysts. The V_2O_5-WO_3/TiO_2 catalysts are known to active in the intermediate and high temperature region (i.e. 200–400 ºC) but the V_2O_5-MoO_3/TiO_2 catalysts have a high activity in the low and intermediate temperature region (i.e. 150–350 ºC). On the other hand, less data are known on the mixed oxides V_2O_5-WO_3-MoO_3/TiO_2 catalysts. In our work we have focused the attention about this three mixed oxides to operate in wider temperature region, the characterization and catalytic activity of V_2O_5-WO_3-MoO_3/TiO_2 model on the catalyst structural and on the reactivity in the SCR reaction.

The presence of other components from the emissions of stationary and mobile sources such as H_2O and SO_2 requires further examination of the catalyst activity. The flue gas compositions as well as temperature also vary with the plant due to different kinds of fuel burnt and operating conditions in each plant. A SCR catalyst designed specifically to the specified flue gas composition and temperature will optimally perform under the design condition.

The amount of loaded vanadium in the investigated catalysts is 3 wt% (base on V_2O_5), the amount of loaded tungsten in the investigated catalysts is varied between 3.5 and 7 wt% (base on WO_3) and the amount of loaded molybdenum in the investigated catalysts is varied between 5 and 10 wt% (base on MoO_3).

The two main objectives of this research are to compare the method of loading metal oxides sequences on the support and calcination sequences to form oxide compounds and finally to find suitable between WO_3 and MoO_3 promoters catalyst composition(s) which will optimally perform with an industrial specification, using powder samples. This research has been scoped as follows:

1. Preparation of TiO_2 support by sol-gel method

2. Preparation of V_2O_5-WO_3-MoO_3 over the TiO_2 support by dry impregnation method

    2.1 Find the appropriate method for catalyst preparation

    2.2 Find suitable composition of WO_3 between 3.5 and 7% (w/w) and MoO_3 between 5 and 10% (w/w)

3. Characterization of catalysts using various techniques

    3.1 Determination of the composition of metal by Inductively coupled plasma optical emission spectroscopy (ICP-OES)

    3.2 Determination of the crystal structure by X-ray diffraction technique (XRD)

3.3 Determination of the surface area based on Brunauer, Emmett and Teller (BET)

3.4 Determination of the acid sites of the synthesize catalysts by NH_3 Temperature   programmed desorption (NH_3-TPD)

3.5 Determination of the functional group on the catalyst surface by Fourier transform Infrared Spectroscopy (FTIR)

4. Measure the catalytic activity at various operating conditions including feed gas concentration over the synthesized catalysts.

The present thesis is organizes as follows:

Chapter I describes background and scopes of the research.

Chapter II presents principles of SCR of NO by NH_3 using V_2O_5 based, V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalysts.

Chapter III describes procedures for the preparation of titanium dioxide, V_2O_5-WO_3-MoO_3/TiO_2 catalysts, experimental system and testing procedures.

Chapter IV presents experimental results and discussion.

Chapter V presents overall conclusions of this research and recommendations for further research.

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter presents previous studies relate to the selective catalytic reduction of NO by ammonia. In this section, we describe the SCR of NO_X by NH_3, the SO_2 oxidation, the active phases and the roles of the support and promoters in the commertial catalysts, V_2O_5–WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 and the effects of the presence of H_2O and SO_2 on NO reaction.

2.1 Selective catalytic reduction (SCR) of NO by ammonia

NO_x emissions can be reduced by a variety of methods. The selective catalytic reduction is one of the most widely used technology to reduce nitrogen oxide emissions from stationary sources. The catalytic flue gas cleaning plays major role worldwide and the trend of industry power plant also pushes forward the development of new flue gas cleaning technologies. The SCR of NO_x with ammonia as a reductant becomes a more attractive commercial solution. This process is based on the reduction of NO_X with NH_3 to produce nitrogen and water according to the two main reactions.

$$4NO + 4NH_3 + O_2 \quad \rightarrow 4N_2 + 6H_2O \qquad \text{(eq. 2.1)}$$

$$2NO_2 + 4NH_3 + O_2 \quad \rightarrow 3N_2 + 6H_2O \qquad \text{(eq. 2.2)}$$
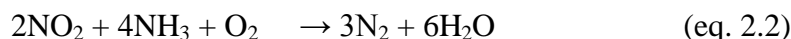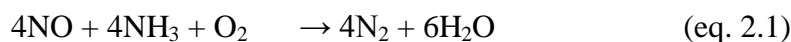
During the SCR reactions, it is known that when the temperature of the SCR reaction increases above about 350°C, NH_3 reacts with oxygen rather than NO to form nitrogen oxides (NO, N_2O), according to the reactions.

$$4NH_3 + 5O_2 \quad \rightarrow 4NO + 6H_2O \qquad \text{(eq. 2.3)}$$

$$2NH_3 + 2O_2 \quad \rightarrow N_2O + 3H_2O \qquad \text{(eq. 2.4)}$$

$$2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O \qquad \text{(eq. 2.5)}$$
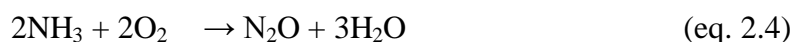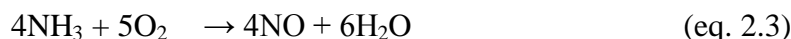
The SCR catalysts should be the material that active as an oxidation catalyst and partial oxidation when supported on tinania. In the past, the vanadium catalyst was first found to be active in the SCR process in 1960s. Today, the most commonly used material for this reaction such as V_2O_5, WO_3 and MO_3.

Jung and Grange (2002) investigated V=O band behavior over V_2O_5 crystallite during the ammonia adsorption and the characterization of SCR reaction. They found that the decreasing of V=O band intensity due to the reduction of V_2O_5 surface and/or the adsorption of NH_3. Under the conditions of SCR reaction, the 70% intensity of original V=O band was preserved up to 300°C. The oxidation state of vanadium was about +4.4. At the high temperature, 400°C, they found that almost all the V=O band was recovered. From these results, they suggested that the oxidation of NH_3 attributed to the increase of two neighboring V=O sites which result in the SCR activity decrease.

Oh (2004) investigated the SCR activity of NO with NH_3 via varying the concentration of oxygen from 0 to 3%. When the experiment are carried out by performing the reaction up to 450ºC, high NO and NH_3 were removed in the presence of a small amount of oxygen. However, the increasing oxygen concentration from 0.1 to 0.3% had no significant effect to the removal of both NO and NH_3 species. They found that the increase of oxygen concentration decreased the N_2O production in the presence of oxygen.

2.2 The SO_2 oxidation

The optimum vanadium loading depends on application types. When the sulfur level in the exhaust gas is high, the vanadium content should be at a lower level so as to prevent the SO_2 oxidation to form SO_3.

Sulfur dioxide can be further oxidized if it presents in the combustion gases. Sulfur dioxide reacts with oxygen to form sulfur trioxide through SO_2 oxidation reaction over V_2O_5 based catalyst. It is known that SO_2 ultimately reacts with NH_3 or catalyst to form a sulfur compound on the catalyst surface following.

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad \text{(eq. 2.5)}$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \qquad \text{(eq. 2.6)}$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \qquad \text{(eq. 2.7)}$$
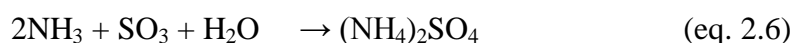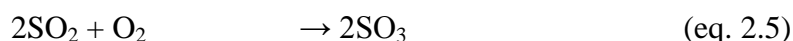
Titania (anatase) based SCR catalyst is preferred to use as support of vanadia due to its resistance to SO_X-poisoning. TiO_2 is only partially and reversibly sulfated on its surface when the SCR reaction takes place in the presence of SO_2. Orsenigo et al. (1998) investigated the role of the surface sulfates in NO_X reduction and SO_2 oxidation on V_2O_5-WO_3/TiO_2 catalysts. They suggested that the formation of sulfates occurred first at the vanadyl sites and later on at the exposed titania surface. Sulfates formation at or near the vanadyl sites increased the reactivity in the de-NO_X reaction, possibly due to the increase in the acidity of the catalyst, whereas the titania surface acted as SO_3 acceptor and affects the outlet SO_3 concentration during catalyst conditioning for the SO_2 oxidation reaction.

In most stationary combustion processes, sulfur trioxide reacts with ammonia reducing agent and H_2O and forms ammonium bisulfate and/or ammonium sulfate, the major deactivating agent. Therefore, inducing deactivation of catalyst. This undesired product will block the pores in the structure of the catalyst and disturb with the reaction of the reactants because they can cause deposition and accumulation of ammonium sulfate salts onto the catalyst (if the temperature of the catalyst is not high enough) and onto the air-pre-heater downstream from the catalytic reactor (Forzatti et al., 2000).

SO$_3$ can form sulfuric acid and ammonium sulfate that cause corrosion and deposition of solid by-products downstream from the reactor. These undesired sulfates can easily fill and block the pores in the catalyst structure and eventually cause severe deactivation of catalysts. The occupation of the active sites by metal sulfates and ammonium sulfates would consequently decrease the SCR activity (Park et al., 2001).

Kamata et al. (2001) studied SO$_2$ oxidation over the V$_2$O$_5$/TiO$_2$ SCR catalyst. They reported that the rate of SO$_2$ oxidation increased almost linearly with V$_2$O$_5$ loading below the monolayer capacity and attained saturation with further increase. This work reported that the hydroxyl groups bonded to vanadium atoms, V$-$OH, might be altered by SO$_2$ oxidation. Both V$=$O and V$-$OH groups involved in the adsorption and desorption of SO$_2$ and SO$_3$.

Boudali et al. (2009) studied characterization and reactivity of WO$_3$-V$_2$O$_5$ supported on sulfated titanium pillared clay catalysts for the SCR-NO reaction. They found that the stability of sulfate depended on the loaded metal oxides and the reduction properties of SO$_4^{2-}$ or V$_2$O$_5$ in the sample were changed in the presence of WO$_3$. Some interaction of sulfate with tungsten and vanadia species on the surface of sulfated Ti-pillared clay support due to the difference in reduction properties of sulfate. Vanadia enhanced the NO removal activity of sulfated Ti-pillared clay, while no significant effect of tungsten was observed for WO$_3$-V$_2$O$_5$/sulfated Ti-pillared clay catalyst. When both tungsten and sulfate exist simultaneously on the surface of vanadia supported sulfated Ti-pillared clay, the sulfate species seemed to play a more important role for NO removal activity than tungsten.

2.3 The active phases and the roles of the support and promoters in the industrial catalysts (Busca et al., 1998)

Since different power plants burn different kinds of fuel and operate at different condition, the flue gas composition as well as temperature also varies with the plant. A SCR catalyst designed specifically to the specified flue gas composition and temperature will optimally perform under the design condition. Several studies have been published concerning the characterization of V$_2$O$_5$-WO$_3$/TiO$_2$ model and

industrial SCR catalysts. On the other hand, fewer data are known on V_2O_5-MoO_3/TiO_2 catalysts. In all cases the best catalysts contain just a few less than a full monolayer of vanadium plus tungsten (or molybdenum) oxides over the anatase TiO_2 support. The reason of TiO_2-anatase as the best support for SCR catalysts relies on two main reasons:

1. SO_2 is usually present in the waste gases of power plants. In the presence of oxygen it can be oxidized to SO_3, thus forming metal sulfate by reacting with the oxide catalyst support. TiO_2 is only weakly and reversibly sulfated in the conditions approaching those of the SCR reaction and the stability of sulfates on the TiO_2 surface is weaker than on other oxides such as Al_2O_3 and ZrO_2. Consequently, TiO_2-based industrial catalysts are only partially and reversibly sulfated at their surfaces upon SCR reaction in the presence of SO_2 and this sulfation even enhances the SCR catalytic activity.

2. The supporting V_2O_5 on TiO_2 anatase leads to very active oxidation catalysts and more active than other supports. The reason for this activity enhancement is a result of the good dispersion of vanadium oxide on TiO_2 giving rise to isolated vanadyl centers and polymeric polyvanadate species.

Therefore, anatase TiO_2 is an activating support, giving rise to catalysts that are stable against sulfation. However, vanadia supported on titania is quite an unstable system. Because at any temperature and pressure, anatase form of titania can transform to the less effective phase, rutile. The anatase-to-rutile phase transformation is favored by addition of V_2O_5, which also favors the anatase sintering and loss of surface area. On the contrary, WO_3 and MoO_3 hinder both surface area loss of anatase and its transformation to rutile. Another reason for their addition to V_2O_5 supported on TiO_2 is effect of such components in undesired SO_2 oxidation. In fact, WO_3 and MoO_3 compete with and displace SO_3 on the basic sites of the TiO_2 surface and tend to cover it, thus limiting its sulfation. Therefore, WO_3 and MoO_3 are used as stabilizers and as promoters of the SCR catalysts and possibly as inhibitors of the SO_2 oxidation.

For V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2, the active sites are vanadium oxide species. In fact W- and Mo- free V_2O_5/TiO_2 is also active and quite selective in SCR, its activity being definitely better than those of WO_3/TiO_2 and MoO_3/TiO_2. The amount of vanadium oxide is variable but generally very small (<1% (w/w)), at least in the most recent catalyst formulations. Indeed, vanadia is responsible for the activity of the catalyst in the NO_X reduction but also for the undesired oxidation of SO_2 to SO_3 in the case of sulfur bearing fuels. WO_3 is employed in a larger amount (about 10% (w/w)) to increase the catalyst activity and thermal stability.

2.4 V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2

Chen and Yang (1992) reported that the promoters such as WO_3 was commonly added to V_2O_5/TiO_2 catalyst to increase the SCR activity. They reported that these promoters preferentially interacted with vanadium oxide species on the titania surface to form two-dimensional surface metal oxides, and then created acid sites on the catalyst surface. The strong interaction between vanadia and tungsten species on the TiO_2 support increased the acidity of TiO_2 and exhibited a higher catalytic activity. WO_3 also increased the poison resistance to alkali and reduces ammonia oxidation. Therefore, the role of WO_3 in the V_2O_5/TiO_2 catalytic system is very important. During the study of the effect of WO_3 on NO reduction activity of SCR catalytic filter, they found that WO_3 significantly improved the catalytic activity at lower temperature and broadens the temperature window of the maximum NO conversion and the addition of WO_3 increased the catalytic activity and broadened the reaction temperature window. A wider reaction temperature window allowed flexibility in operation of the reaction. The addition of WO_3 also significantly enhanced the poison resistance of V_2O_5-based catalyst toward alkali metal oxides that were the strongest SCR poisons.

Paganini et al. (1997) studied evidence for the existence of interactions between vanadium and tungsten surface species by catalytic tests in the SCR reaction. The catalytic measurements have shown that V_2O_5-WO_3/TiO_2 samples were more active in NO conversion than V_2O_5 /TiO_2 and WO_3/TiO_2 samples with the same

vanadium or tungsten loading, maintaining a high selectivity to N_2 even at high temperature where almost complete NO consumption occurred.

Nova et al, (1998) reported that the MoO_3/TiO_2 catalysts were active in the reduction of NO by NH_3, the reactivity of the catalysts increased when the MoO_3 loading increased. Whereas the formation of undesired N_2O caused the N_2 selectivity decreased. The formation of N_2O was primarily ascribed to a reaction between NH_3 and NO, and not to the ammonia oxidation reaction. A comparison with a WO_3/TiO_2 catalyst having similar molar composition indicated that the WO_3- and MoO_3- containing samples exhibit similar structural and morphological characteristics, but different reactivity: the WO_3/TiO_2 sample is less active but more selective in the SCR reaction.

Casagrande et al. (1999) studied the SCR of NO by NH_3 over TiO_2-supported V_2O_5–MoO_3 catalysts. They found that the ternary V_2O_5–MoO_3/TiO_2 catalysts were more active in the SCR reaction at low temperatures compared to the corresponding binary samples. The 'temperature window' of the reaction was widened and shifted towards lower temperatures. There transient reactivity data provided clear evidence in favor of the hypothesis of a redox mechanism for the SCR reaction and pointed out that the ternary catalysts were more easily reduced and reoxidized than the corresponding binary samples. This indicated that the simultaneous presence of vanadium and molybdenum enhanced the catalyst redox properties, and thus its reactivity. They reported that their conclusions were also in line with the results of the characterization studies pointing out the existence of electronic interactions involving the vanadium and molybdenum surface oxide species. They also indicated that the effects of the addition of WO_3 and MoO_3 to V_2O_5/TiO_2 were similar, both oxides acting as 'chemical' promoters besides playing a 'structural' function as well.

Reiche et al. (2000) studied titania-supported V_2O_5-WO_3 catalysts in the selective reduction of NO by NH_3. They reported that increasing of the calcination temperature from 300 to 500°C decreased the activity of catalysts with low loading. This behavior was attributed to spreading of the vanadia species over the titania surface, resulting in an increase of less active monomeric vanadyl species. For

catalysts with higher loading, the interaction between vanadia and tungsta species was intensified with increasing calcination temperature, affording higher activity and new species with hydroxyl groups. In contrast, no correlation was observed between the activity and the ease of reduction of the catalysts by ammonia. Strong interaction between vanadia and tungsta species resulted in a higher activity compared to the corresponding titania-supported single oxides. The studies demonstrated that high activity could be achieved with ternary V_2O_5-WO_3/TiO_2 catalysts if the total loading exceeds an experimental monolayer and the catalyst was calcined at 500°C, or with catalysts derived from WO_3/TiO_2 calcined at 800°C, before vanadia deposition.

Kleemann et al. (2000) investigated the ammonia adsorption on monolithic SCR catalysts, containing either V_2O_5–WO_3/TiO_2 or V_2O_5/TiO_2. The experiments have shown that the addition of WO_3 was essential for achieving low ammonia slip under practical operating conditions. The superior properties of catalysts containing WO_3 were due to several positive effects of WO_3. It was found that under typical SCR conditions the ammonia surface coverage was significantly higher on a WO_3-containing catalyst. The high acidity of WO_3 also led to an increased amount of strongly adsorbed ammonia, thus improving the catalytic activity especially at low ammonia partial pressures. Finally, the researchers suggested that the ammonia transport to the active sites is enhanced by close interaction of WO_3 with V_2O_5.

Djerad et al. (2004) studied titania-supported tungsten and vanadia oxides with different W and V loadings and calcined at different temperatures. All samples have been prepared by the sol–gel method. They reported that large amount of tungsten (9%; w/w) provided thermal stability to WO_3/TiO_2 systems upon addition of vanadia. It is found that WO_3 and V_2O_5 crystallites were formed when their concentrations were higher than those corresponding to three monolayers. Differential thermal analysis have shown that the presence of V_2O_5 crystallites was not essential for the transformation of titania anatase into rutile. High reactivity in limited temperature range (225–350°C) has been observed for the catalyst with 8%(w/w) V_2O_5 with a high formation of N_2O amount during the SCR reaction. The catalyst with 3%(w/w) V_2O_5 exhibited a slight lower reactivity but with a high selectivity to N_2 preserved in all working temperature. High vanadia loading decreased the

temperature required for conversion of titania anatase into rutile. Increasing vanadia loadings led to the sintering of the TiO_2 support and to aggregation of isolated vanadium ions which favored the activity in the SCR reaction but only in a narrow temperature window and promoted the undesired ammonia oxidation at high temperatures.

Djerad et al. (2006) studied the effect of oxygen concentration on the NO_X reduction with ammonia over V_2O_5–WO_3/TiO_2 catalyst. Their results have shown that the selective catalytic reduction was strongly affected by the varying 2-15 vol% of oxygen concentration in low temperature range (150–275°C). At higher temperatures, the reaction became independent of the O_2 concentration. The rate of the selective catalytic reduction of NO with ammonia may be considerably enhanced by converting part of the NO into NO_2. DRIFT measurements have shown that NH_3 and NO_2 were adsorbed on the catalyst surface on the contrary of NO. The experiments have shown that the decrease in N_2 selectivity of the SCR reaction was mainly due to the selective catalytic oxidation of ammonia and to the formation of nitrous oxide.

2.5 The effect of the presence of H_2O and SO_2 on NO reduction

Lietti et al. (2000) studied selective catalytic reduction (SCR) of NO by NH_3 over TiO_2-supported V_2O_5–WO_3 and V_2O_5–MoO_3 catalysts. Their data indicated that WO_3 and MoO_3 behaved as "structural" and "chemical" promoters for the catalysts. MoO_3-based catalysts were more active but less selective than WO_3–V_2O_5/TiO_2 catalysts in the SCR reaction, although in the presence of water the catalytic performances of the investigated samples were comparable.

Long and Yang (2000) investigated selective catalytic reduction of NO with ammonia over V_2O_5 doped TiO_2 pillared clay catalysts. They revealed that H_2O and SO_2 slightly increased the activities at high temperatures (>350°C) for the V_2O_5/TiO_2-pillared clay catalysts. Addition of WO_3 to V_2O_5 further increased the activities of the pillared clay catalysts. These results indicated that TiO_2-pillared clay was a good support for vanadia catalysts for the SCR reaction. In situ FT–IR experiment indicated that both Brønsted acid sites and Lewis acid sites exist on the catalyst

surface, but with a large proportion being Brønsted acid sites at low temperatures. The reaction path for NO reduction by NH_3 on the V_2O_5/TiO_2-pillared clay was similar to that on V_2O_5/TiO_2 catalyst.

Nova et al. (2000) studied dynamics of SCR reaction over a TiO_2-supported vanadia–tungsta commercial catalyst and found that the presence of low concentrations of water in the feed stream did not seem to affect the ammonia adsorption–desorption process on the surface but significantly inhibited the SCR reaction. An inhibiting effect of adsorbed NH_3 on the SCR reaction was also pointed out.

Huang et al. (2002) investigated effects of H_2O and SO_2 on V_2O_5/activated carbon catalysts for NO reduction with ammonia at lower temperatures and found that in the absence of SO_2, H_2O inhibited the catalytic activity, which may be attributed to competitive adsorption of H_2O and reactants (NO and/or NH_3). In the absence of H_2O, a small amount of ammonium-sulfate salts deposited on the surface of the catalyst, which promoted the SCR activity. However, the deposition rate of ammonium-sulfate salts was much greater, which resulted in blocking of the catalyst pores and deactivated the catalyst. Decreasing V_2O_5 loading decreased the deactivation rate of the catalyst. The catalyst could be used stably at a space velocity of 9000 h^{-1} and temperature of 250°C.

Lin and Bai (2003) studied surface acidity over vanadia/titania catalyst in the selective catalytic reduction for NO removal. The results indicated that the strength of Brønsted acidity positively increased with V_2O_5 loading, whereas Lewis acidity remained almost constant at a typical SCR operating temperature. Water vapor did not affect the adsorption of Lewis ammonia, but the formation of Brønsted acidity has to be accompanied by water vapor adsorption. Brønsted acidity was decreased with increasing temperature and disappeared at a temperature of around 500°C for all testing catalysts, while Lewis acidity slightly decreased with increasing temperature. The disappearance of Brønsted acidity at a high temperature was related to the loss of adsorbed water vapor.

Qi and Yang (2003) studied selective catalytic reduction of NO with NH_3 at low-temperature over iron and manganese oxides supported on titania. It was found that the addition of iron oxide not only increased the NO conversion and N_2 selectivity but also increased the resistance to H_2O and SO_2. H_2O had slight effects on the SCR activity over iron and manganese oxides supported on titania at low temperature.

Tang et al. (2007) studied low temperature selective catalytic reduction of NO_X with NH_3 over amorphous MnO_X catalysts. The result indicated that the decrease in activity by H_2O and SO_2 are due to their competing adsorption with the reactant over the catalysts surface. However, most experimental work on the ammonia adsorption has been performed without water in the feed gas. Water has a strong influence on the ammonia adsorption because it competes with ammonia for the adsorption sites and the activity recovers to the initial level after removing H_2O and SO_2 gases.

2.6 Comment on the previous works

From the above previous works of the SCR process, the SCR catalyst, should be the material that active as an oxidation catalyst and partial oxidation when supported on titania, especially V_2O_5. According to the component in the feed gas include SO_2 which results in the SO_2 oxidation to form the sulfur compound. This undesired product can cause the deactivation of catalyst. However, the sulfates formation at or near the vanadyl sites increases the SCR reactivity due to the increase in the acidity (Orsenigo et al., 1998). Therefore, titania (anatase) based SCR catalyst is preferred to use support of vanadia due to several reason (Busca et al., 1998);

- If compare with other supports, TiO_2 is only weakly and reversibly sulfated in the conditions approaching those of the SCR reaction and the stability of sulfates on the TiO_2 surface is weaker than on other oxides such as Al_2O_3 and ZrO_2.

- The supporting V_2O_5 on TiO_2 anatase leads to very active oxidation catalysts and more active than other supports.

However, the V_2O_5/TiO_2 is not a stable system. At any temperature and pressure, TiO_2 can transform anatase to rutile phase. Therefore, the several works study the addition of metal oxides, WO_3 and MoO_3, hinder both surface area loss of TiO_2 and its transformation to rutile phase. Moreover, WO_3 and MoO_3 are used as stabilizers and as promoters of SCR catalysts and possible as inhibitors of SO_2 oxidation.

The commercial catalysts for SCR process are based on V_2O_5/TiO_2 mixed with WO_3 or MoO_3 using ammonia as a reducing agent. For the V_2O_5-WO_3/TiO_2, this reaction requires a higher temperature in the range of 300–400 ℃ to obtain the desired removal efficiency of NO_x (Beretta et al, 1998 and Kaewbuddee, 2009) and for the V_2O_5-MoO_3/TiO_2 requires a lower temperature in the range of 150–350 ℃ for stationary source in order to minimize energy consumption (Taweesuk, 2011). For the reason mentioned above, we are strongly interested in developing three mixed metal oxides (V_2O_5-WO_3-MoO_3) in order to develop our high active catalysts to find to find the optimal catalyst for various conditions.

For the gas composition, due to different power plants burn different kinds of fuel and operate at different condition, the flue gas composition as well as temperature also varies with the plant. A SCR catalyst designed specifically to the specified flue gas composition and temperature will optimally perform under the design condition. In our work, we use gas composition from the real power plant that consist of 120 ppm NO, 120ppm NH_3, 15%vol O_2, 15%mol H_2O and 30ppm SO_2. This condition is different from the literatures reviewed above. In addition, the content of O_2 concentration in our work is the high content when compare with the previous reviews. The literatures reviewed above one can see the SCR of NO_x by NH_3 over 3% V_2O_5 - 9% WO_3 supported on TiO_2 (Djerad et al., 2006). It indicate that the selectivity towards N_2 decreases with an increased oxygen level. This condition of reaction are 500 ppm NO, 500ppm NH_3 and varying 2, 6, 10, 15%vol O_2. Therefore, in our work using 15%vol of O_2 may occur the high of oxidation reaction to form of NO_x.

CHAPTER III

EXPERIMENTAL

The experimental details in this chapter is divided into three major parts: (3.1) catalyst preparation, (3.2) catalyst characterization and (3.3) schematic diagram of the apparatus and reaction study.

3.1 Catalyst preparation

3.1.1 Chemicals

All chemicals used in this preparation procedure of V_2O_5-WO_3-MoO_3/TiO_2 catalysts are listed in Table 3.1.

Table 3.1 The chemicals used in the catalyst preparation.

Chemical	Supplier
Titanium (IV) isopropoxide	Aldrich
Ammonium metavanadate, 99.99%	Aldrich
Ammonium metatungstate hydrate, 99.99%	Aldrich
Ammonium molybdate tetrahydrate, $\geq$99.0%	Aldrich
Nitric acid 65%	Aldrich
Oxalic acid hydrate	Fluka

3.1.2 Preparation of TiO$_2$ by a sol-gel method

Titanium dioxide was prepared by using a sol-gel method using titanium isopropoxide as precursor. First, 83.5 ml of titanium isopropoxide was dissolved with 7.51 ml of nitric acid 65% in 1000 ml of de-ionized water and then was stirred for 3 days. The obtained clear sol was dialyzed by cellulose membrane in de-ionized water in order to adjust pH to be 3.5. The obtained dialyzed titania sol was dried at 110°C for 24 hours, crushed, grinded, and then calcined at 350°C for 2 hours.

3.1.3 Preparation of V$_2$O$_5$ over TiO$_2$ catalyst

Vanadium, tungsten and molybdenum are loaded to the prepared TiO$_2$ support by incipient wetness method. First, ammonium metavanadate was dissolved with oxalic acid anhydrous in de-ionized water. This pore-filling solution was dropped on TiO$_2$ surface until reaching incipient wetness point. The obtained pore-saturated TiO$_2$ powder was dried at 110°C over night, crushed, grinded and then calcined in air at 500°C for 2 hours.

Ammonium metamolybdenate hydrate and ammonium metatungstate hydrate are impregnated on the obtained product V$_2$O$_5$/TiO$_2$ following the three method listed below. See the example calculation for the catalyst preparation in Appendix B. The details of all catalysts were used in experimental are shown in table 3.2.

3.1.4 Preparation of WO_3 and MoO_3 over V_2O_5/TiO_2 catalyst Method I

First, ammonium metatungstate hydrate was dissolved in de-ionized water. This pore-filling solution was dropped on V_2O_5/TiO_2 surface until reaching incipient wetness point. The obtained pore-saturated powder was dried at 110°C over night, crushed, grinded and then calcined in air at 500°C for 2 hours. Finally, ammonium metamolybdenate hydrate was dissolved in de-ionized water. This pore-filling solution was dropped on V_2O_5-WO_3/TiO_2 surface until reaching incipient wetness point. The obtained pore-saturated powder was dried at 110°C over night, crushed, grinded and then calcined in air at 500°C for 2 hours. The sequence of loading metal oxides is following:

Figure 3.1 The sequence of loading metal oxides Method I.

3.1.5 Preparation of WO₃ and MoO₃ over V₂O₅/TiO₂ catalyst Method II

First, ammonium metamolybdenate hydrate was dissolved in de-ionized water. This pore-filling solution was dropped on V_2O_5/TiO_2 surface until reaching incipient wetness point. The obtained pore-saturated powder was dried at 110°C over night, crushed, grinded and then calcined in air at 500°C for 2 hours. Finally, ammonium metatungstate hydrate was dissolved in de-ionized water. This pore-filling solution was dropped on V_2O_5-MoO_3/TiO_2 surface until reaching incipient wetness point. The obtained pore-saturated powder was dried at 110°C over night, crushed, grinded and then calcined in air at 500°C for 2 hours.

V_2O_5/TiO_2

Ammonium metamolybdenate hydrate

Calcination for V_2O_5-MoO_3/TiO_2

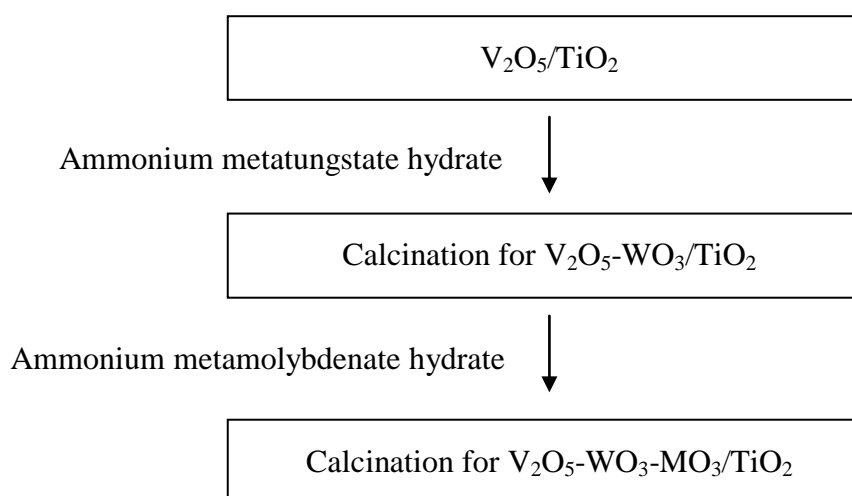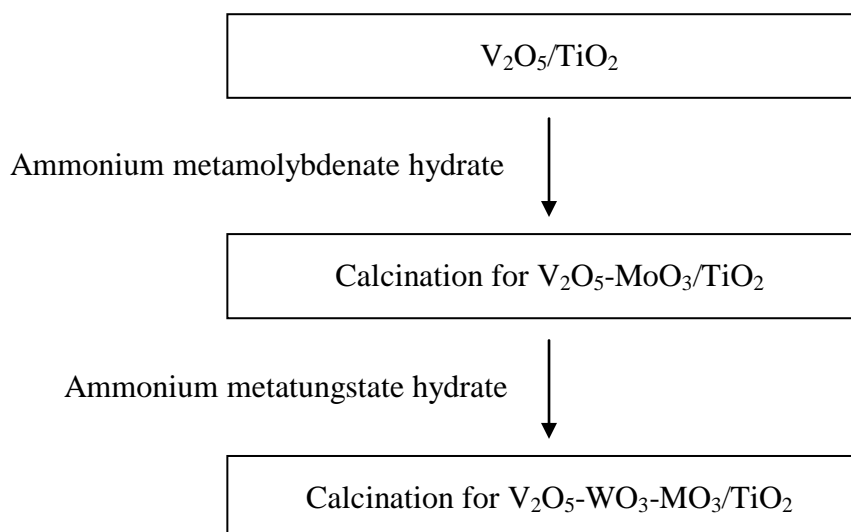Ammonium metatungstate hydrate

Calcination for V_2O_5-WO_3-MO_3/TiO_2

Figure 3.2 The sequence of loading metal oxides Method II.

3.1.6 Preparation of WO$_3$ and MoO$_3$ over V$_2$O$_5$/TiO$_2$ catalyst Method III

First, ammonium metatungstate hydrate and ammonium metamolybdenate hydrate were dissolved in de-ionized water. This pore-filling solution was dropped on V$_2$O$_5$/TiO$_2$ surface until reaching incipient wetness point. The obtained pore-saturated powder was dried at 110°C over night, crushed, grinded and finally, calcined in air at 500°C for 2 hours.
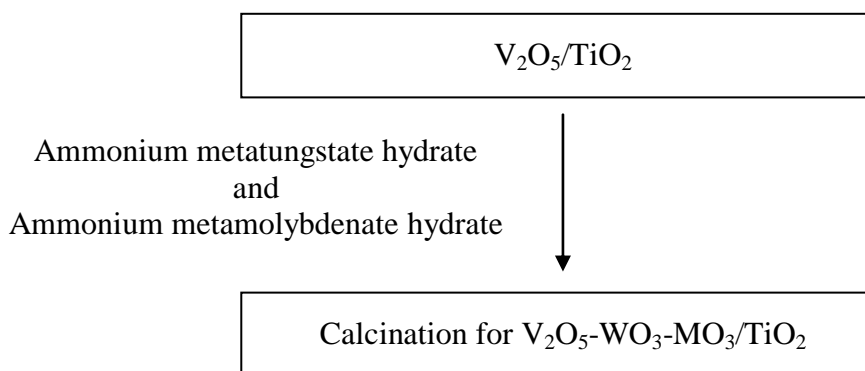
Figure 3.3 The sequence of loading metal oxides Method III.

Table 3.2 The details of all catalysts used in experiments.

Symbol	Compositions V$_2$O :WO$_3$:MoO$_3$	Method	1st Calcination Temperature (°C)	2nd Calcination Temperature (°C)	3rd Calcination Temperature (°C)
3V7W10Mo#1	3 : 7 : 10	I	500	500	500
3V7W10Mo#2	3 : 7 : 10	II	500	500	500
3V7W10Mo#3	3 : 7 : 10	III	500	500	-
3V7W5Mo#2	3 : 7 : 5	II	500	500	500
3V3.5W10Mo#2	3 : 3.5 : 10	II	500	500	500
3V3.5W5Mo#2	3 : 3.5 : 5	II	500	500	500

3.2 Characterization of catalysts

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

The percentage of metal loading of each catalyst prepared in this study was analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The amount of metal on the surface of titanium dioxide was measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES) Perkin Elmer model PLASMA-1000. About 0.02 g (weight to an exact amount) of catalyst was dissolved in 10 ml hydrofluoric acid 49%, stir until all solid are solution then make volume up to 100 ml using de-ionized water by the volumetric flask which has the volume of 100 ml. The concentration of the sample after volume adjustment is about 1-24 ppm (mg/l).

3.2.2 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by using D8 Advance of Bruker AXS. The experiments were carried out by using CuKα radiation. Scans were performed over the 2Ө ranges from 20° to 80° with step size 0.02^{o}/sec and slit width 0.6 nm. The XRD spectrum is used to identify the crystal structure of the catalyst.

3.2.3 BET surface area measurement

The specific surface area was determined by nitrogen adsorption method. The specific surface area of the catalysts was measured by Micromeritrics ASAP 2020 using nitrogen as the adsorbate. The operating conditions were 200°C for degasing temperature. The sample cell contained 0.2 g of sample.

3.2.4 NH$_3$ Temperature programmed desorption (NH$_3$-TPD)

Temperature programmed desorption (TPD) using NH$_3$ performed in BELCAT-A at PTT Research & Technology Institute. The amount of NH$_3$ adsorbed on the surface was determined by thermal conductivity detector.

The catalyst sample, approximately 0.05 gram of sample was placed in quartz tube in a temperature-controlled furnace. Helium gas with a flow rate 50 ml/min was fed through sample. The sample was heated from a room temperature to 500 °C with a heating rate of 10 °C/min and held for one hour to remove moisture. Then the sample was cooled down to 100 °C. After that, 10% volume of NH$_3$ in balance helium gas was flowed through sample at a flow rate of 50 ml/min and held for 30 minutes. Subsequently, helium gas was flowed through sample at flow rate of 50 ml/min for 45 minutes. Finally, the sample was heated from a room temperature to 500 °C with a heating rate of 10 °C/min. The signal from this step was recorded every one second and stored on a microcomputer.

3.2.5 Fourier transforms Infrared (FT-IR)

The functional group on the catalyst surface is determined by FT-IR using Nicolet model Impact 6700 of the IR spectrometer. Infrared spectra are recorded between 400 and 4000 cm^{-1} on a microcomputer.

3.3 Catalytic activity measurement

In this study, the activity testing of catalysts is divided into dry and wet conditions. The SCR of NO by NH_3 over V_2O_5-WO_3-MoO_3/TiO_2 catalysts under dry and wet condition in the reaction temperature range of 100-450°C is presented. The reaction mixture consisted of 120 ppm NO, 120 ppm NH_3, 15 vol.% O_2 with a balance of N_2. Catalytic activity test is carried out in a tubular fixed-bed reactor.

The reactor used is a 7 mm ID stainless tubular fixed bed reactor. An electric furnace is used to supply heat to the reactor. Temperature of the furnace is controlled by a digital temperature controller. The diagram of the system is exhibited schematically in Figure 3.4. The total flow rate of feed gas mixture is about 200 ml/min. Flow rate of each feed gas stream is controlled by using a set of mass flow controllers. In each run about 0.1 g of the prepared catalyst is tested by passing the feed gas stream through the catalyst bed packed on quartz wool. In this research, there are two phases to evaluate the NO_X concentration in the effluent gas. NO_X concentration in the outlet stream is measured by an online NO_X analyzer (NOA-7000, SHIMADZU). NH_3 concentration is analyzed using a gas chromatograph Shimadzu GC-2014 equipped with a pulsed discharge detector (PDD)

In the initial phase of the research, the performance of the investigated catalyst were evaluated from the concentration of NO in the effluent gas by an online NO_X analyzer (NOA-7000, SHIMADZU). NO conversion is calculated from the following equation.

$$\% \text{ NO conversion} = \frac{\text{NO conc. in feed} - \text{NO conc. in effluent gas}}{\text{NO conc. in feed}} \times 100 \quad \text{(eq. 3.1)}$$

In the second phase of the research, due to the break down of the NO analyzer NOA-7000, the performance of the investigated catalysts were evaluated from the amount of NH_3 reacted with NO using a gas chromatograph Shimadzu GC-2014 equipped with a pulsed discharge detector (PDD). NH_3, however, can also be oxidized to NO by O_2 also. Two experiments, therefore, have to be performed to quantify the amounts of NH_3 consumed by the oxidation with O_2 and the reaction with NO. Both

experiments used the same operation conditions reported below but no NO is fed in the run used to quantify the amount of NH_3 oxidized by O_2.

In the second phase, the conversion of NO can be calculated using the following steps.

$$NH_3 \text{ converted} \quad = \quad NH_3 \text{ inlet - } NH_3 \text{ outlet} \qquad \text{(eq. 3.2)}$$

In the reaction having no NO (NH_3 oxidation reaction)

$$NH_3 \text{ oxidized by } O_2 \quad = \quad NH_3 \text{ converted} \qquad \text{(eq. 3.3)}$$

In the reaction having NO (SCR reaction)

$$NH_3 \text{ reacted with NO} \quad = \quad NH_3 \text{ converted - } NH_3 \text{ oxidized by } O_2 \qquad \text{(eq. 3.4)}$$

Assume NH_3 and NO reacted ratio 1:1 molar ratio

$$NO \text{ in the effluent gas } (NO_{out}) \quad = \quad NO_{in} \text{ - } NH_3 \text{ reacted with NO}$$
$$+ \, NH_3 \text{ oxidized by } O_2 \qquad \text{(eq. 3.5)}$$

$$\text{Therefore,} \quad \% \text{ NO conversion} \quad = \quad \frac{NO_{in} - NO_{out}}{NO_{in}} \times 100 \qquad \text{(eq. 3.6)}$$

Reaction condition for test of SCR activity:

Flow rate	200 ml/min
Temperature	100–450 °C
[NO]	120 ppm
[NH_3]	120 ppm
[O_2]	15 % v/v
[H_2O]	15 % mol
[SO_2]	30 ppm
Nitrogen	balance

Flow meter

Valve

Check Valve

Saturator and heater

O$_2$

Valve

Valve

SO$_2$

N$_2$

Reactor
and
furnace

By pass

Temperature
controller

Valve

NO

NH$_3$

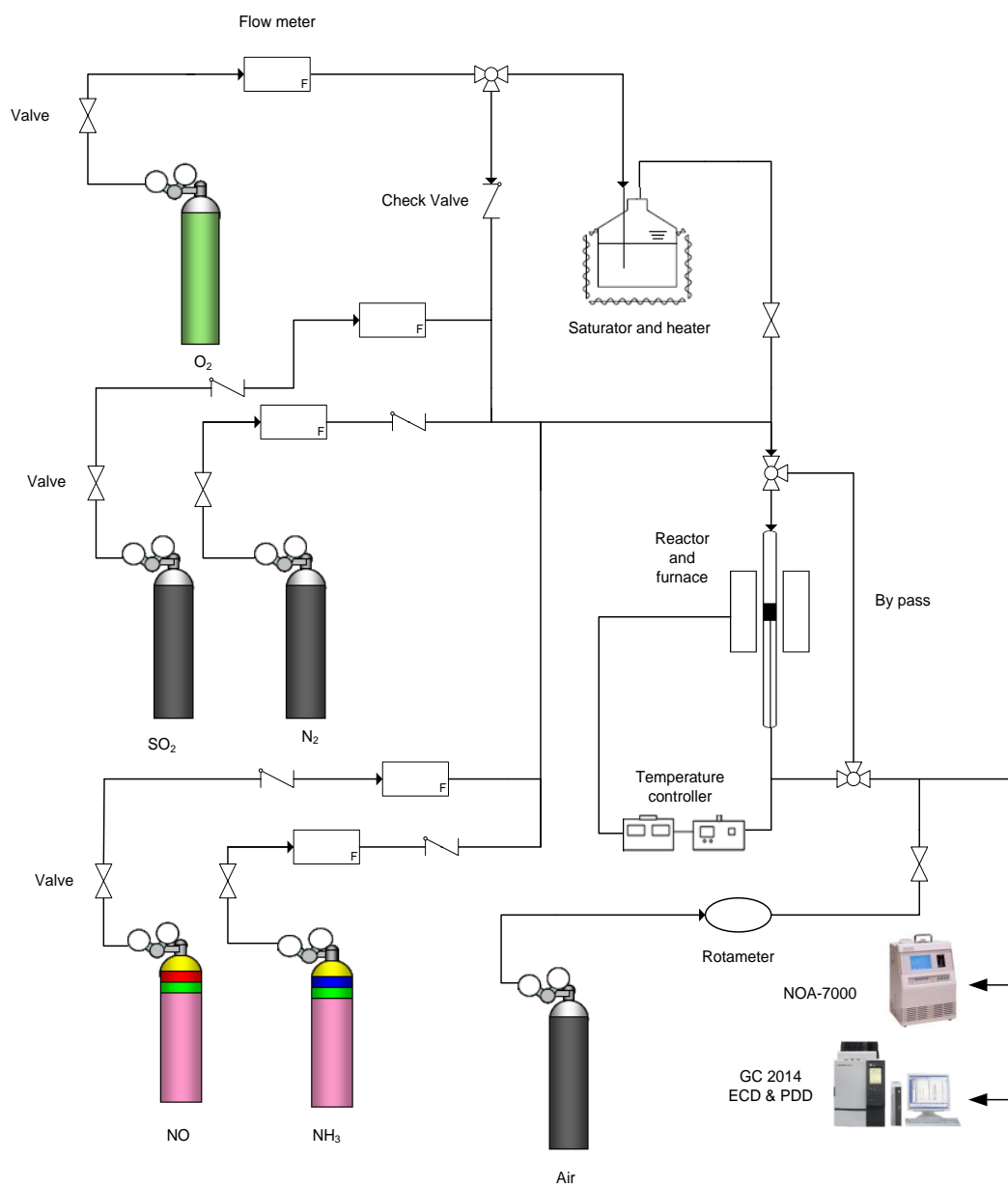Air

Rotameter

NOA-7000

GC 2014
ECD & PDD

Figure 3.4 Flow diagram of the reactor system for SCR of NO by NH$_3$.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter the experimental results obtained from the selective catalytic reduction of nitrogen oxide by ammonia over V_2O_5-WO_3-MoO_3/TiO_2 catalysts are reported. This chapter is divided into two main parts. The first part, section 4.1, discusses the results of various characterization techniques for catalyst properties. The second part, section 4.2, discusses activity of V_2O_5-WO_3-MoO_3/TiO_2 catalysts in different conditions. The catalytic activities are reported as a function of reaction temperature.

4.1 Characterization of V_2O_5-WO_3-MoO_3/TiO_2 catalysts

In this section, the prepared V_2O_5-WO_3-MoO_3 catalysts are characterized by ICP-OES to determine the amounts of metal loading of catalyst, XRD to analyze crystal structure, nitrogen adsorption to determine specific surface area, NH_3-TPD to determine amounts of acid site on the catalyst surface and FT-IR to determine the functional group on the catalyst surface. The catalytic activity is measured as NO conversion in the reaction temperature ranging from 100 to 450°C.

4.1.1 Composition of vanadium, tungsten and molybdenum of V_2O_5-WO_3-MoO_3/TiO_2

Amounts of vanadium, tungsten and molybdenum loading were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The compositions of the SCR catalysts are displayed in Table 4.1.

Table 4.1 The compositions of V_2O_5-WO_3-MoO_3/TiO_2 catalysts.

Catalyst Sample	Vanadium oxide content (%wt.)	Tungsten oxide content (%wt.)	Molybdenum oxide content (%wt.)
3V7W10Mo#1	3.2	7.2	10.5
3V7W10Mo#2	3.2	6.9	10.6
3V7W10Mo#3	3.3	7.8	10.7
3V7W5Mo#2	3.1	7.4	5.3
3V3.5W10Mo#2	3.1	3.4	10.3
3V3.5W5Mo#2	3.3	3.8	5.7

4.1.2 X-ray diffractometry

The XRD patterns of various V_2O_5-WO_3-MoO_3/TiO_2 catalysts are shown in Figures 4.1. The results indicate that all the catalysts contained anatase TiO_2 primarily while the small amounts of rutile and brookite phases are also presence. However, no peak of V_2O_5, WO_3 and MoO_3 appears in any XRD patterns at different levels of WO_3 and MoO_3 content. The disappearance of XRD patterns of other compounds apart from TiO_2 indicates that V, W and Mo may not form a crystal structure or they may form oxide structures having crystal size too small to be detected by XRD.
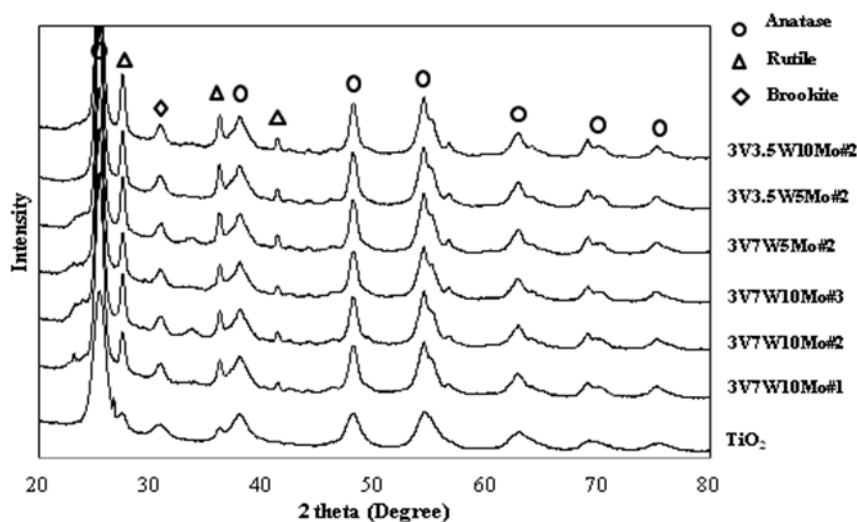
Figure 4.1 XRD patterns of V_2O_5-WO_3-MoO_3/TiO_2 catalysts.

4.1.3 Specific surface area of catalysts

The most common procedure for determining surface area of a solid is based on the adsorption and condensation of nitrogen at the boiling point temperature of liquid nitrogen. This method employed BET (Brunauer-Emmett-Teller) isotherm to calculate the surface area. About 0.2 grams of catalyst used in measurement. BET surface areas of the catalysts are listed in Table 4.2. The BET surface areas of the SCR catalysts are lower than that of titania (90.9 m^2/g), possibly due to the SCR catalysts are calcined several times. The BET surface area versus the WO_3 and MoO_3 loading increases progressively from 43.7 to 47.8 m^2/g, as the promoter content decrease from 7 to 3.5 wt. % WO_3 and 10 to 5 wt. % MoO_3 respectively. This is possibly due to the formed WO_3 and MoO_3 block some pore of the support of catalyst. Therefore, the decreasing of promoter contents increase the surface area of SCR catalysts.

Table 4.2 BET surface areas of the V_2O_5-WO_3-MoO_3/TiO_2 catalysts.

Catalyst Sample	BET surface area (m^2/g)
TiO_2	90.9
3V7W10Mo#1	39.1
3V7W10Mo#2	43.7
3V7W10Mo#3	40.2
3V7W5Mo#2	44.0
3V3.5W10Mo#2	45.2
3V3.5W5Mo#2	47.8

4.1.4 Temperature programmed desorption using NH$_3$ as a probe molecule (NH$_3$-TPD)
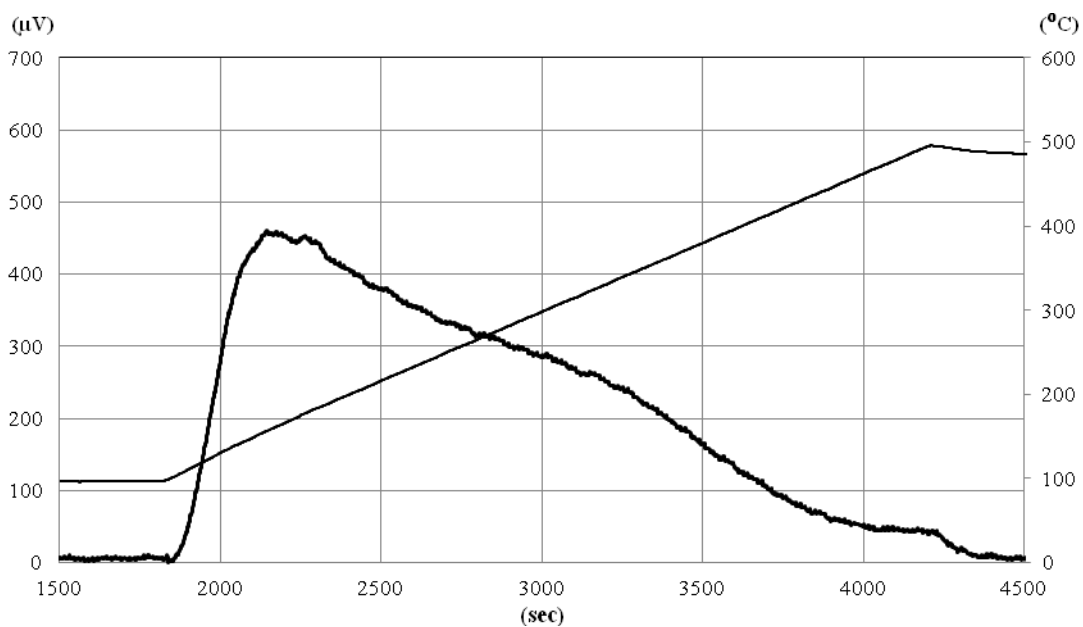
Temperature program desorption is a commonly used technique for the determination of amount and strength of surface acid sites. The strength of an acid site can be qualitatively related to the corresponding desorption temperature of ammonia while the amount of all the acid sites and strong acid cites can be quantitatively determined from the amount of NH$_3$ the sample can adsorb. The amounts of these acid sites are calculated from the area under the curve and are listed in Table 4.3 and in Figures 4.2–4.8.

It should be noted here that before the adsorption of NH$_3$, the catalysts samples were subjected to surface cleaning by heating at 500ºC in a He stream for 1 hour. Therefore, the surfaces of the samples should be cleared from any adsorb gases and, especially, water. The removal of water from the surface means that any Bronsted acid sites, if originally exist may be removed also. The adsorption of NH$_3$, hence, should mainly occur on Lewis acid site, i.e. metal cations which are Ti^{4+}, V^{m+}, W^{n+} and Mo^{p+}. Because of this reason, the total amount of NH$_3$ the catalyst surface can adsorb can be used as a rough indicator represents the total number of metal cation exposes on the catalyst surface.

Figures 4.2–4.8 show the amount of all acid sites of all catalysts including TiO$_2$ support, that are calculated from the area under the curve of desorption. The results show the two peaks in NH$_3$-TPD profiles. The first obviously peak is found in all figures including TiO$_2$ support but the second peak is not found in the TiO$_2$ support profile. The second peak shows the strong acid sites that bring to the occurring reaction. In addition, the comparison of the amount of acid sites necessary to consider in the acid strength. A large amount of acid sites with a low acid strength occur a reaction less than a small amount of acid sites with a high acid strength. However, the acid strength relate to NH$_3$-TPD temperature. Therefore, we also consider the second peak to find the acid strength of all catalyst with the NH$_3$-TPD temperature.

Table 4.3 Amounts of acid site on various V_2O_5-WO_3-MoO_3/TiO_2 catalysts.

Catalyst Sample	Amounts of acid site (μmol H^+/g)	Amounts of strong acid site (μmol H^+/g)
TiO_2	377	-
3V7W10Mo#1	378	94
3V7W10Mo#2	385	91
3V7W10Mo#3	380	88
3V7W5Mo#2	388	78
3V3.5W10Mo#2	390	87
3V3.5W5Mo#2	379	78

Figure 4.2 NH$_3$-TPD profiles of TiO$_2$ support.
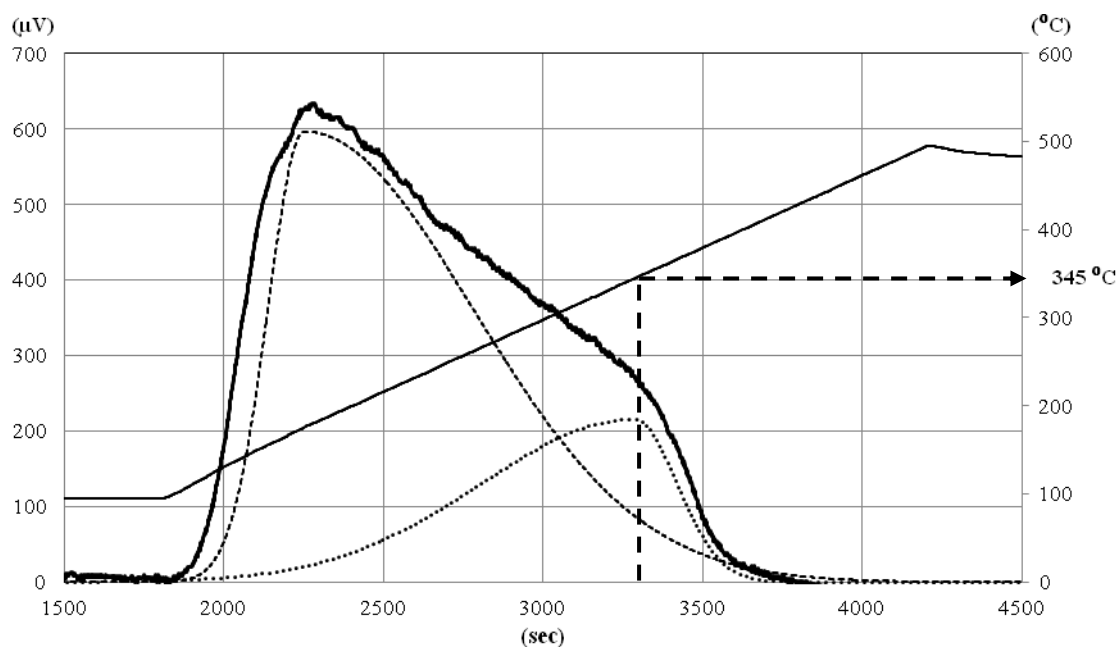
Figure 4.3 NH$_3$-TPD profiles of 3V7W10Mo#1 catalyst.
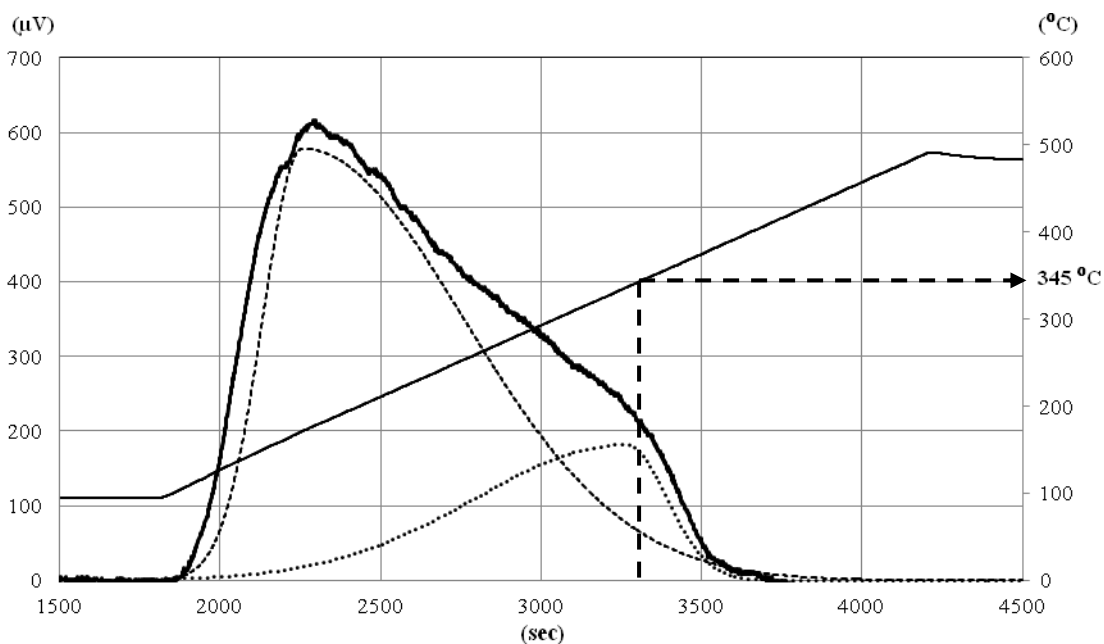
Figure 4.4 NH$_3$-TPD profiles of 3V7W10Mo#2 catalyst.
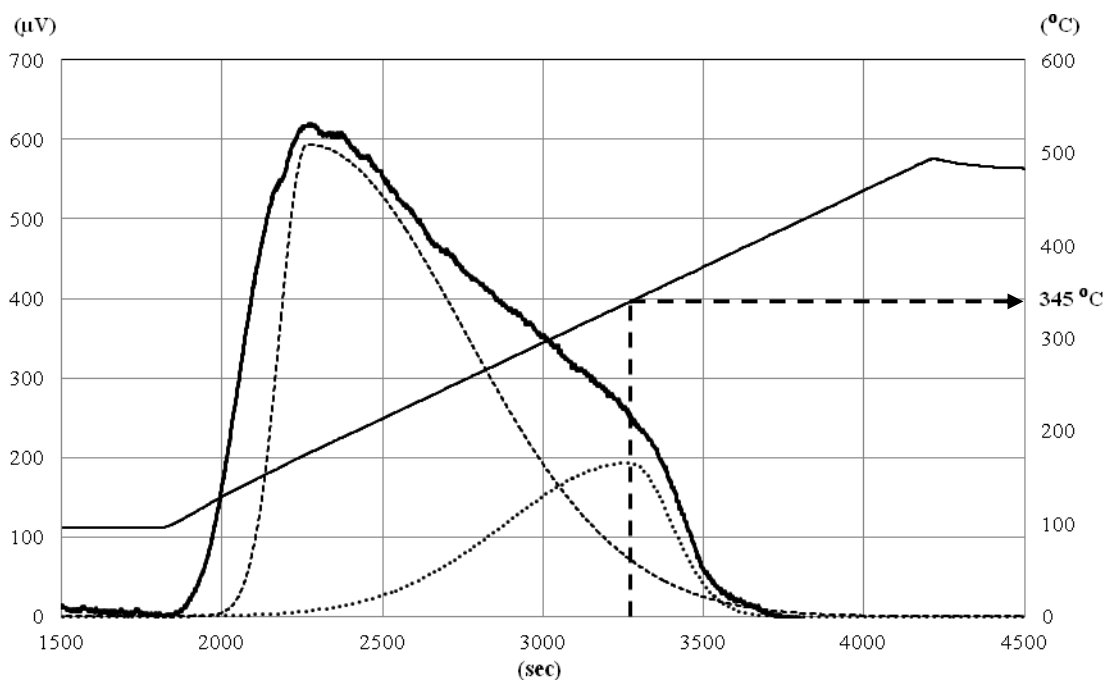
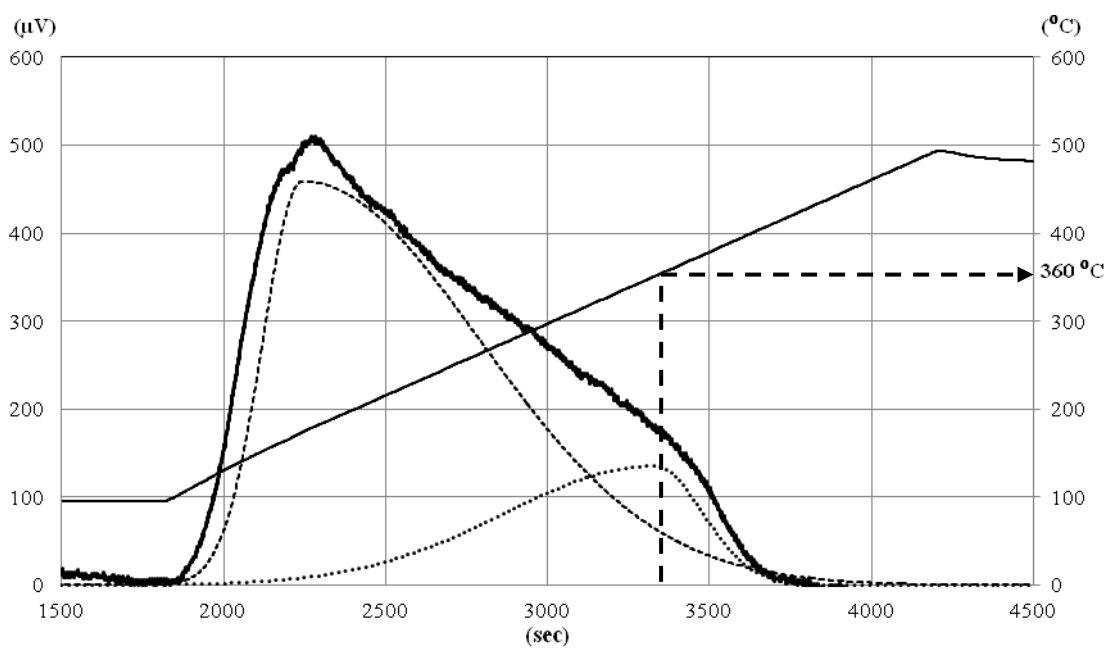**Figure 4.5** NH$_3$-TPD profiles of 3V7W10Mo#3 catalyst.

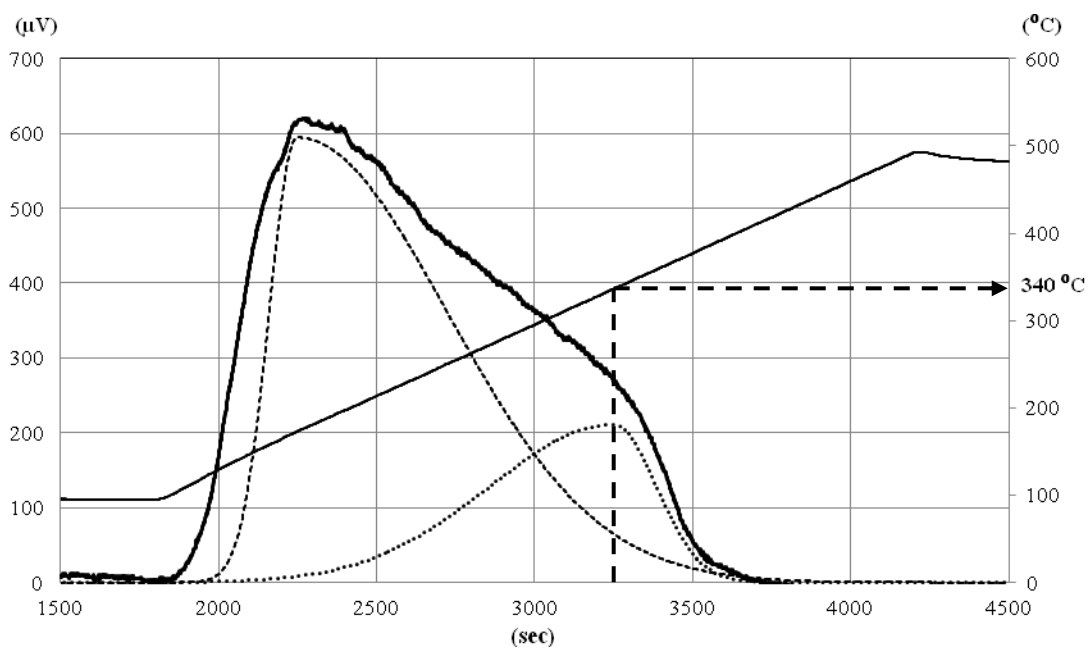**Figure 4.6** NH$_3$-TPD profiles of 3V7W5Mo#2 catalyst.

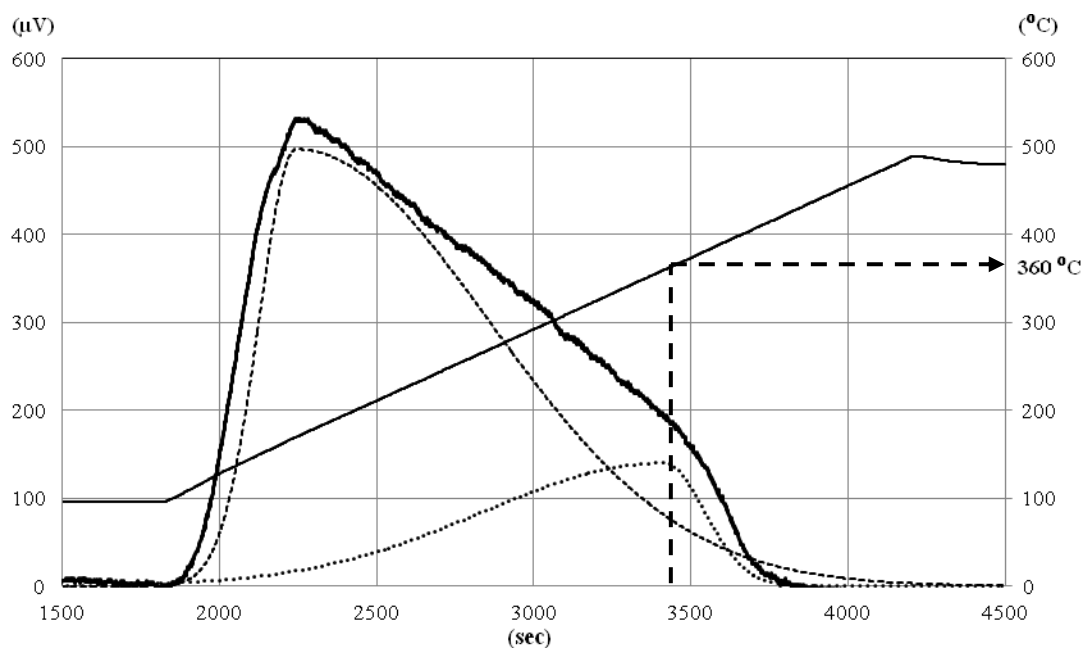**Figure 4.7** NH$_3$-TPD profiles of 3V3.5W10Mo #2 catalyst.

Figure 4.8 NH$_3$-TPD profiles of 3V3.5W5Mo #2 catalyst.

Please refers to data in Table 4.3. TiO_2 and the SCR catalysts have about the same number of surface acid site. TiO_2, however, has surface area about two times higher than the surface area of the SCR catalysts. This result means that the addition of V, W and Mo doubles the density of the acid sites on the surface of the SCR catalyst. It is surprising to find that all the SCR catalysts have about the same number of surface acidic site despite the fact that the amount of metal loaded different significantly. For example, 3V7W10Mo#2 catalyst has higher load of Mo and W two times than 3V3.5W5Mo#2 catalyst, both catalysts have about the same number of surface acidic sites, ie. 385 and 379 μmol H^+/g respectively.

The small variation on the total number of surface acidic sites of the SCR catalysts despite significant changes on the amount of Mo and W loading suggests that the oxides of Mo and W prefer to form on their former oxides species rather than on TiO_2 surface. Figure 4.9 graphically explains this phenomenon.
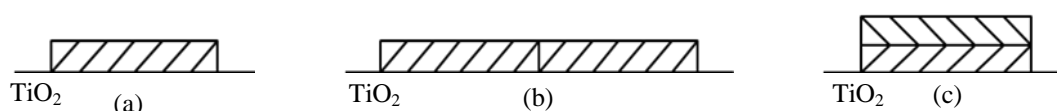

Figure 4.9 Graphically of the phenomenon on V_2O_5-WO_3-MoO_3/TiO_2 catalyst surface.

(a) oxide loading x%

(b) oxide loading 2x%, in this case the surface area of the loaded metal oxide increases twice. Therefore, the number of surface acidic site should increase twice also.

(c) oxide loading 2x%. In this case the surface area of the loaded metal oxide does not significantly increase. Therefore, the amount of surface acidic site is about the same as of oxide loading x%.

Figure 4.9 (a) shows a case when we have x% of a metal oxide on TiO_2 surface. When the metal oxide loading is increased to 2x%, if the metal oxide forms as shown in figure 4.9 (b), the total surface area of the loaded metal oxide will increase. This will lead to higher number of surface acidic site. On the contrary, if the metal oxide (2x%) forms as shown in figure 4.9 (c), the total surface area of the loaded metal oxide does not increase. This will cause no change on the total number of acidic sites.

From NH_3-TPD results, the increasing of acidity is an advantage point for selective catalytic reduction of NO by NH_3 since the NH_3 must adsorb to vanadium site of catalyst (Busca et al., 1998).

From Figures 4.2-4.8, considering in the form of the acid strength, the results show that all profiles have the second peak that present the acid strength excepting TiO_2 support profile. These are indicate that the loading of two promoters, W and Mo, promote the SCR activity.

4.1.5 Functional group on the catalyst surface

The FT-IR spectra (KBr pressed disks) of the V_2O_5-WO_3-MoO_3/TiO_2 catalysts are shown in figures 4.10-4.15. Three peaks of the all spectra are reported in the 400-1200 cm^{-1} range. The results show two strong absorption at 707 cm^{-1}, the typical of TiO_2 anatase and 764 cm^{-1}, the W=O stretching of wolframyl species. The weak band on the shoulder near 974 cm^{-1} is assigned to the composite oxide of vanadium and molybdenum. In addition no peak of V_2O_5 and MoO_3 passed absorption band.
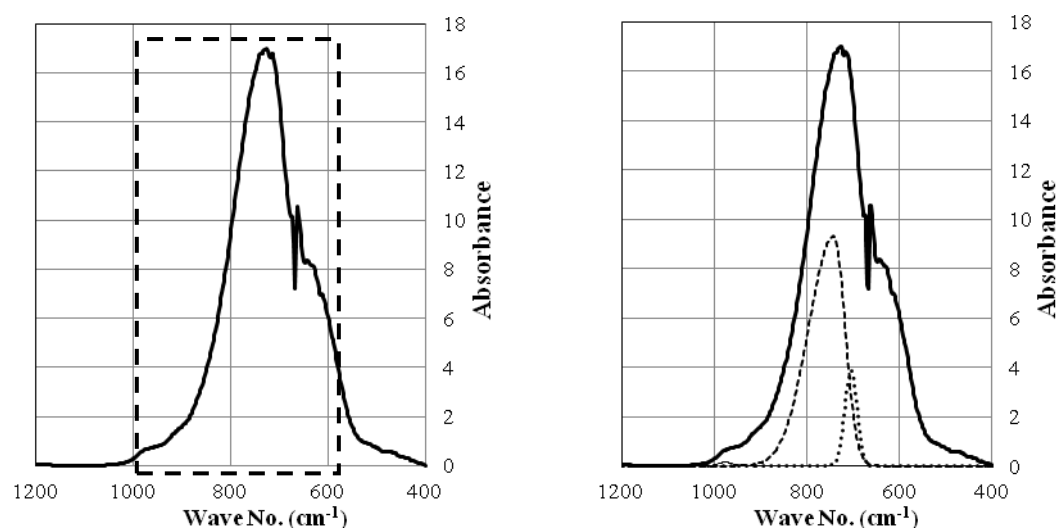

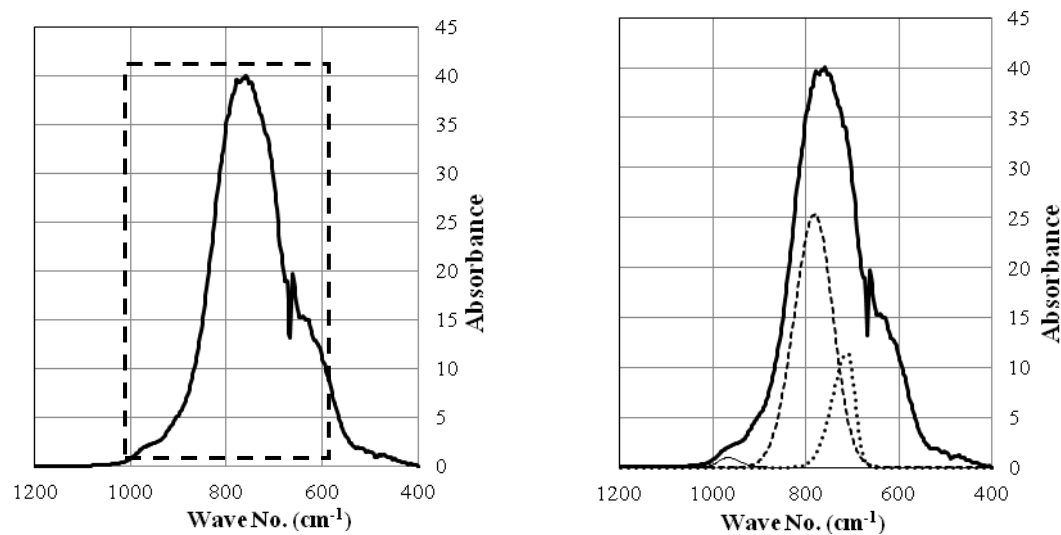**Figure 4.10** FT-IR spectra of 3V7W10Mo#1 catalyst.

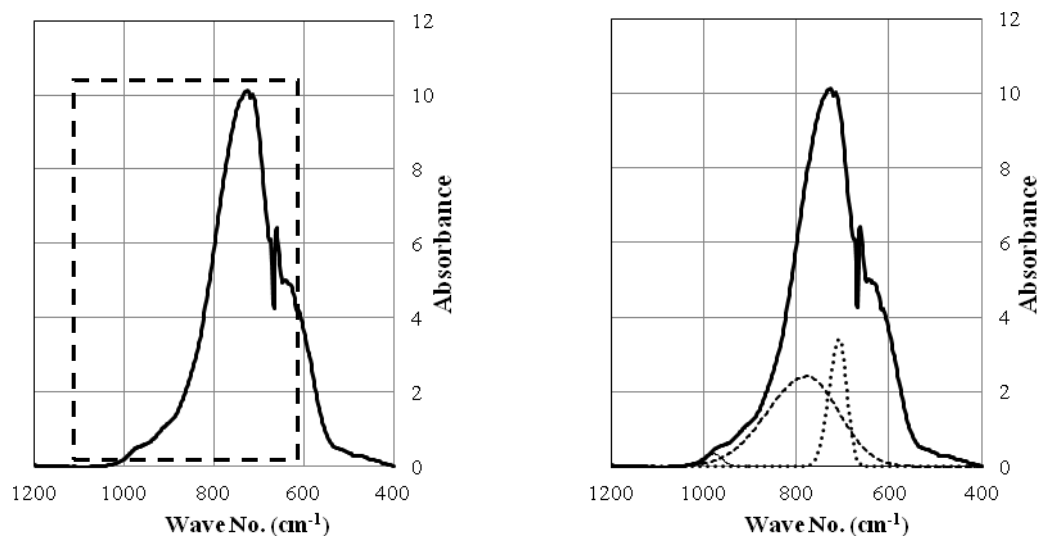**Figure 4.11** FT-IR spectra of 3V7W10Mo #2 catalyst.

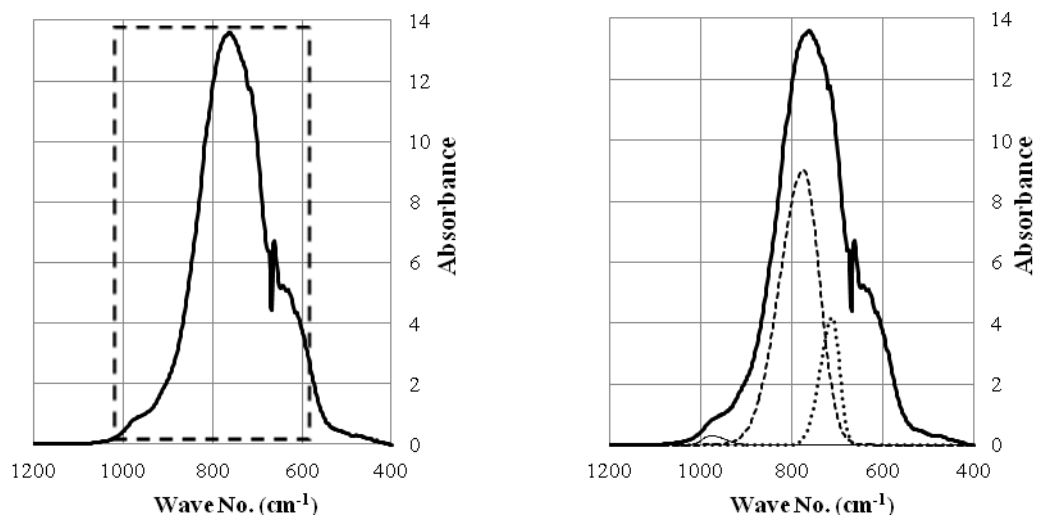**Figure 4.12** FT-IR spectra of 3V7W10Mo#3 catalyst.

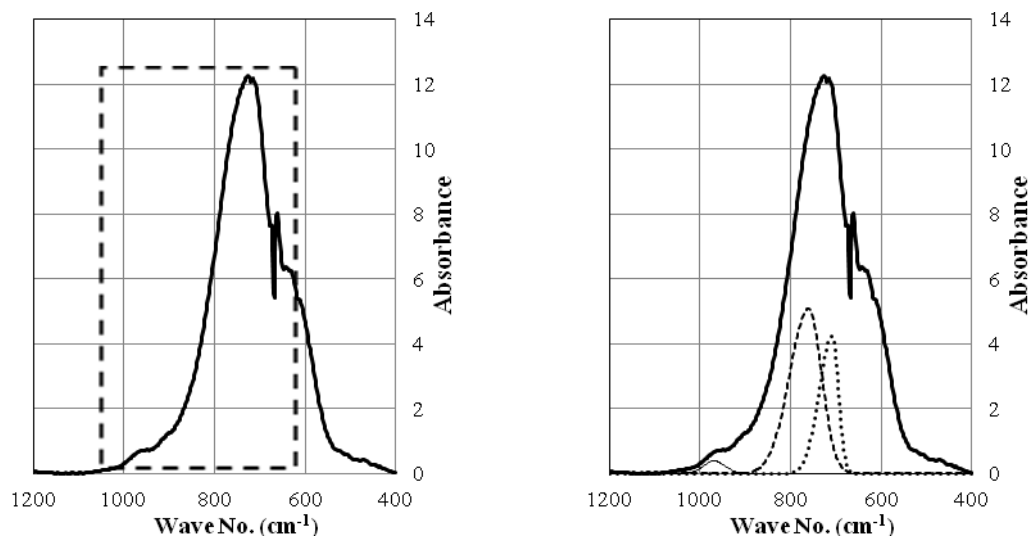**Figure 4.13** FT-IR spectra of 3V7W5Mo#2 catalyst.
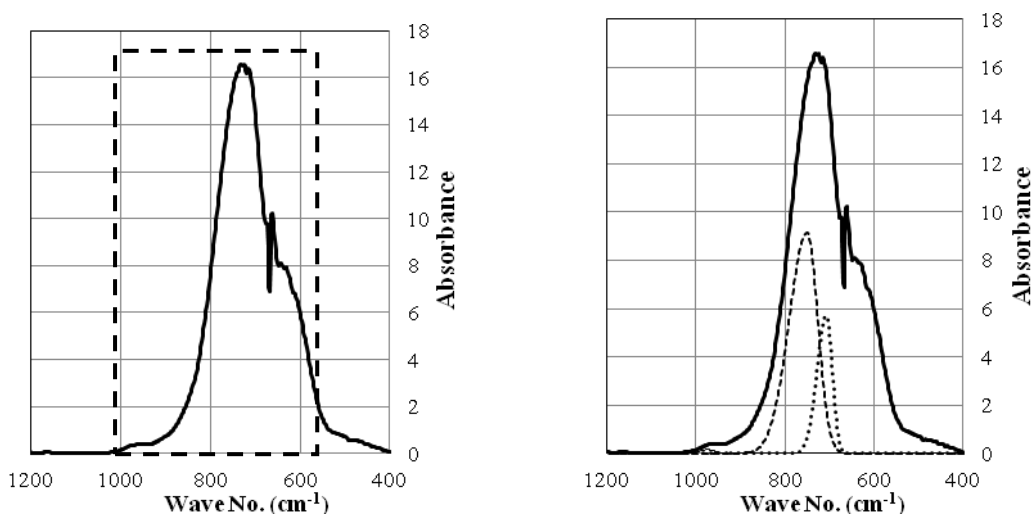
Figure 4.14 FT-IR spectra of 3V3.5W10Mo#2 catalyst.

Figure 4.15 FT-IR spectra of 3V3.5W5Mo#2 catalyst.

4.2 Selective catalytic reduction of NO by NH_3 over V_2O_5-WO_3-MoO_3/TiO_2 catalysts

This section presents the catalytic activities of V_2O_5-WO_3-MoO_3/TiO_2 catalysts in four parts. The first part, section 4.2.1, presents NO conversion of V_2O_5-WO_3-MoO_3/TiO_2 catalysts by various loading metal oxides sequences and calcinations sequences in order to find a suitable method of catalyst preparation by considering stability the catalysts.

The second part, section 4.2.2, compares the combined effect of H_2O and SO_2 on the activity of the two selected catalysts from the first part that gives rise to high NO conversion. In addition, the effect of H_2O and SO_2 on the selected catalysts.

The third, section 4.2.3, the catalyst having optimum method of preparation selected from the first and the second parts, are evaluated by changing W and Mo loading in order to find a suitable composition between MoO_3 and WO_3 promoters catalyst composition(s) that gives rise to high NO conversion.

The last part, section 4.2.4, compares the activity of V_2O_5-WO_3/TiO_2, V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3-MoO_3/TiO_2 with V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 which were studied in previous research.

4.2.1 Effect of loading metal oxides sequences and calcinations sequences on the activity of V_2O_5-WO_3-MoO_3/TiO_2

The results of SCR activity over V_2O_5-WO_3-MoO_3/TiO_2 catalysts prepared from various methods in the reaction temperature range of 100-450°C are presented in this section. The composition of feed gas stream is 120 ppm NO, 120 ppm NH_3, 15 vol. % O_2, and balancing N_2. The catalytic activities of V_2O_5-WO_3-MoO_3/TiO_2 are illustrated in Figures 4.16-4.19. The first run is the run without H_2O and SO_2 from 100°C to 450°C. Then the catalyst bed is allowed to cool down to 100°C before the second run, the run without H_2O and SO_2 was performed again. The catalyst used in the first run is re-used again in the second run. NO_x analyzer Shimadzu NOA-7000 is used to measure NO concentration in the effluent gas.

An objective of repeating two runs without changing the catalyst is to check the repeatability of the experiment and the stability of the prepared catalysts. The repeatability is considered from the profile and the difference between NO conversions of the NO conversion–reaction temperature curves obtained from two successive runs. If the shapes of the two profiles obtained from two successive runs are the same and the discrepancy between two profiles is not much, the catalyst is considered to be stable and the experiment is considered to be repeatable also.

The discrepancy between two profiles is also used as a criterion to judge whether the difference observed is significant or not. If the difference observed is smaller than the discrepancy between the obtained two profiles, that difference is considered insignificant.

- 3V7W10Mo#1:

This catalyst is prepared by following the procedures given in section 3.1.4. This catalyst is calcined at 500°C for 2 hours, 3 times (after adding V, after adding W and finally after adding Mo).
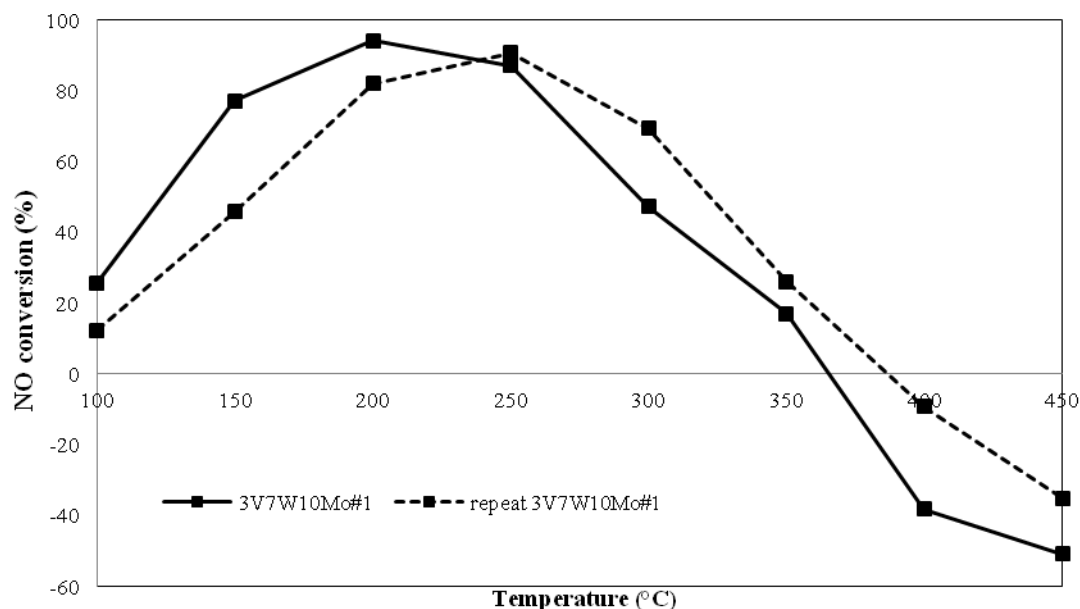
Figure 4.16 The SCR activity over 3V7W10Mo#1/TiO$_2$ catalyst. Reaction conditions: [NH$_3$] = [NO] = 120 ppm, [O$_2$] = 15%, WHSV = 120,000 ml/g-h.

The result in Figure 4.16 shows that the NO conversion-reaction temperatures profiles obtained from the first run and the second run are different significantly. The cause of the difference is likely due to the incomplete formation of the oxide structure on the TiO$_2$ surface. During the reaction of the first run at high temperature, the transformation continues. Therefore, the oxide structure on the catalyst surface at the beginning of the first run and the second run is different. This result is a pronounce change in the NO conversion-reaction temperature profile of this catalyst.

- 3V7W10Mo#2:

This catalyst is prepared by following the procedures given in section 3.1.5. This catalyst is calcined, at 500°C for 2 hours, 3 times (after adding V, after adding Mo and finally after adding W).

The results in Figure 4.17 indicate that the SCR activity increases with the reaction temperature and remains high in the reaction temperature range 200-300°C before decreasing. The profile of the second run is similar to that of the first run but slightly lower. This catalyst, however, is considered stable after the preparation.

In addition, when the reaction temperature is further raised beyond 300°C, the NO conversion in the effluent gas rapidly drops due to the occurrence of the NH_3 oxidation reaction which generates NO. The NH_3 oxidation of this catalyst is the lowest of all catalysts since the NO conversion of this catalyst remain positive in the high reaction temperature region.
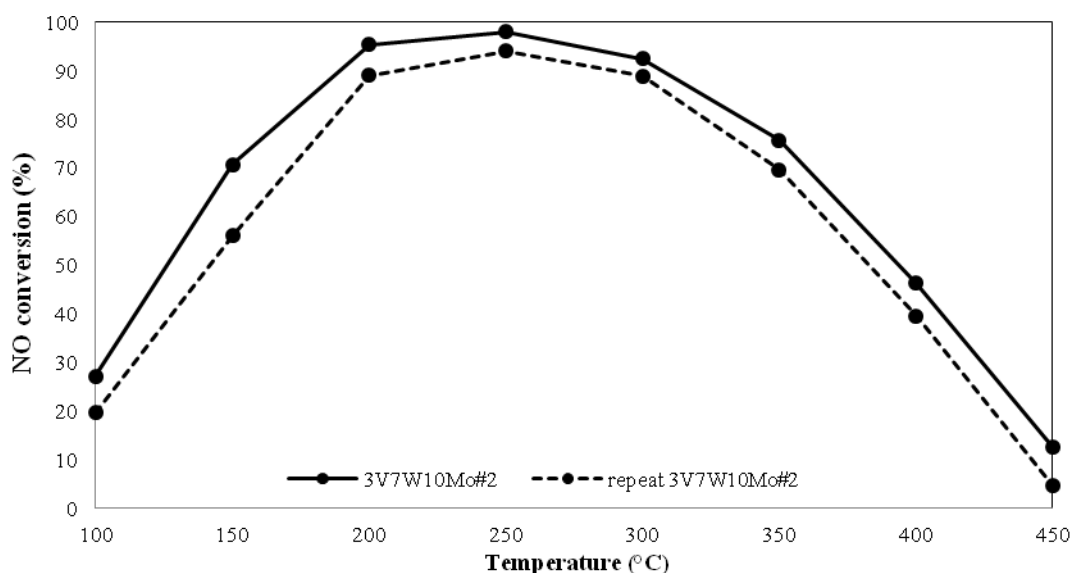

Figure 4.17 The SCR activity over 3V7W10Mo#2/TiO_2 catalyst. Reaction conditions: $[NH_3] = [NO] = 120$ ppm, $[O_2] = 15\%$, WHSV = 120,000 ml/g-h.

- 3V7W10Mo#3:

This catalyst is prepared by following the procedures given in section 3.1.6. This catalyst is calcined, at 500°C for 2 hours, only twice (after adding V and after adding W and Mo). The result in Figure 4.18 shows that the NO conversion increases with the reaction temperature and remains high in the reaction temperature range 200-300°C before decreasing.

This catalyst has high stability due to the profile of the second run is very similar the profile of the first run. However, the NH_3 oxidation of this catalyst is higher than that of 3V7W10Mo#2.
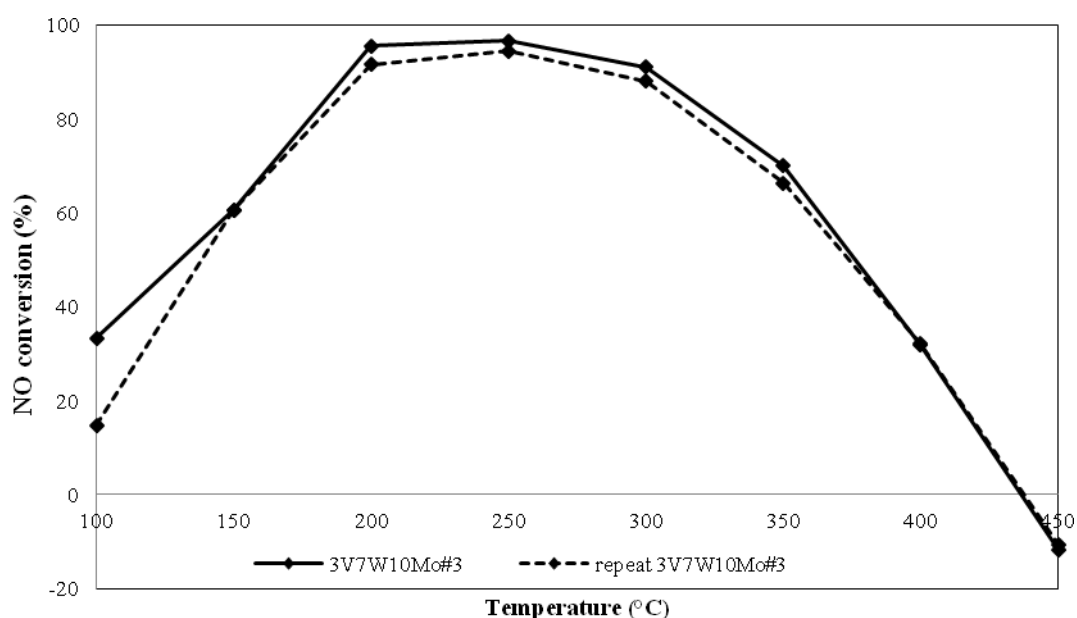

Figure 4.18 The SCR activity over 3V7W10Mo#3/TiO$_2$ catalyst. Reaction conditions: [NH$_3$] = [NO] = 120 ppm, [O$_2$] = 15%, WHSV = 120,000 ml/g-h.

The six profiles showed in Figures 4.16-4.18 are plotted altogether in Figure 4.19. 3V7W10Mo#2 and 3V7W10Mo#3 have comparative activity while 3V7W10Mo#1 has the lowest activity. Therefore, only 3V7W10Mo#2 and 3V7W10Mo#3 are further studied. Their results are reported in next sections.
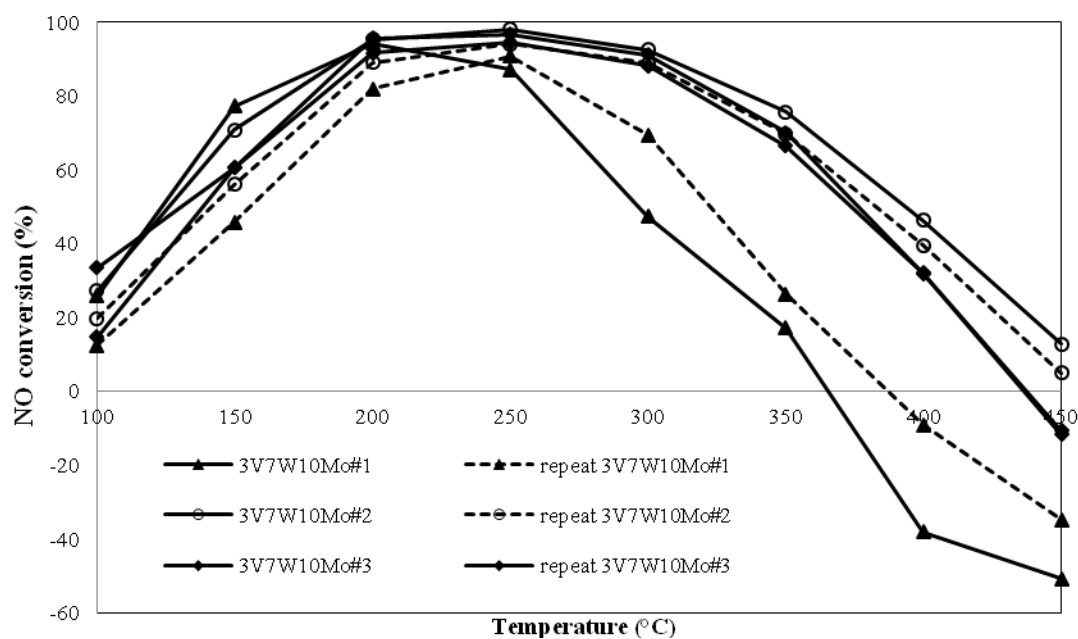

Figure 4.19 The SCR activity over V_2O_5-WO_3-MoO_3/TiO_2 catalysts having various method of preparation. Reaction conditions: $[NH_3] = [NO] = 120$ ppm, $[O_2] = 15\%$, WHSV = 120,000 ml/g-h.

4.2.2 Effect of H_2O and SO_2 on the activity of V_2O_5-WO_3-MoO_3/TiO_2

In this section the activity of all catalysts are investigated in the presence of H_2O and SO_2 in the feed gas. H_2O and SO_2 are main components in flue gases that often interfere the function of catalysts. Therefore, resistance of $DeNO_x$ catalysts to deactivation by H_2O and SO_2 is very important for industrial application. We, therefore, have to further study the effect of H_2O and SO_2 on the SCR activities of our catalyst.

The first thing is to determine the effect of H_2O and SO_2 on the oxidation reaction between NH_3 and oxygen without catalyst. In this study, 120 ppm of NH_3, 15 %mol of H_2O and 30 ppm of SO_2 is fed to the reactor having TiO_2 packed inside. NO_x analyzer Shimadzu NOA-7000 is used to measure NO concentration in the effluent gas.

The NO conversions from the oxidation of NH_3 are illustrated in Figure 4.20. The results indicated that the oxidation of NH_3 to NO can occur at temperature above 300 °C. The experimental results show that the presence of H_2O and SO_2 can reduce the oxidation of NH_3 to NO. It is believed that H_2O and SO_2 can competitively adsorb with NH_3 on the site which can oxidize NH_3 to NO. The adsorption of H_2O and SO_2 block site position of NH_3 oxidation which result in lower NH_3 oxidation reaction. This is the reason why NO concentrations under the presence of H_2O and SO_2 condition above 300°C are lower than without H_2O and SO_2 condition.
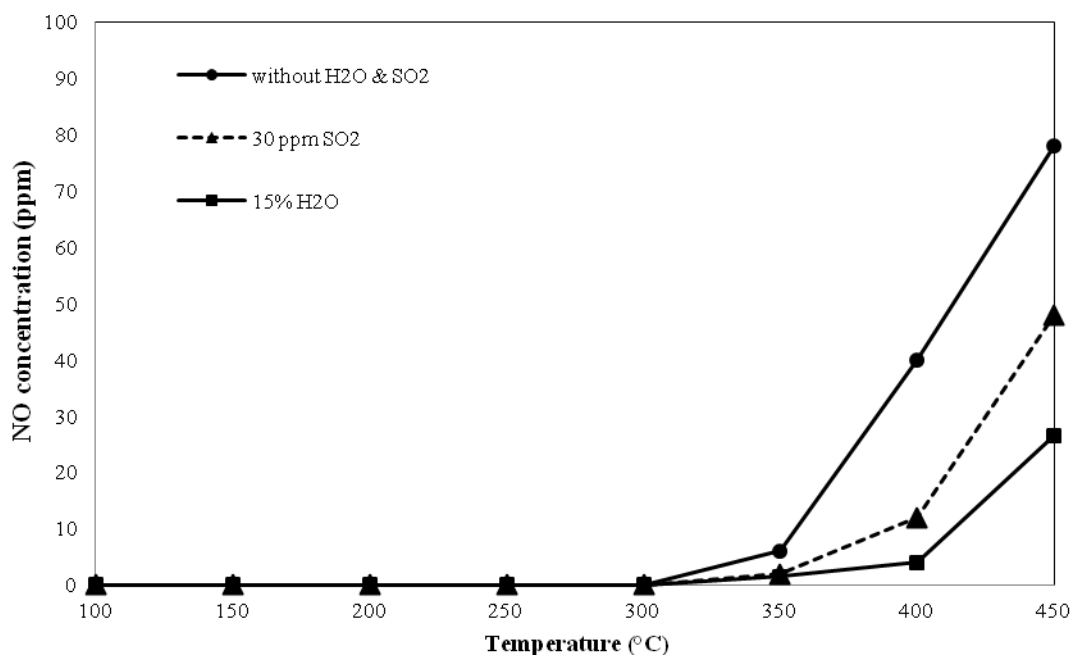
Figure 4.20 The NO concentration from the oxidation of NH_3. Reaction conditions: $[NH_3] = 120$ ppm, $[O_2] = 15\%$, N_2 balance and WHSV = 120,000 ml/g-h.

The combined effect of H_2O and SO_2 on SCR activity of 3V(7W10Mo)#2 and 3V(10)7W#3 catalysts are illustrated in Figures 4.21-4.23. The first run is the run without H_2O and SO_2 from 100°C to 450°C obtained from the section 4.2.1. Then the catalyst bed is allowed to cool down to 100°C before the second run, the run with H_2O and SO_2 was performed.

- 3V7W10Mo#2:

The experimental result in Figure 4.21 shows that when H_2O and SO_2 present in the feed gas, at low temperature the NO conversions are lower than no present H_2O and SO_2. But at high temperature the NO conversions are slightly higher than without H_2O and SO_2. This effect is possibly due to the competitive adsorption of H_2O and SO_2 with NH_3 on the catalyst surface, which reduces the number of sites available for SCR reaction. This brings down the $DeNO_x$ activity at lower temperatures but leads to higher NO conversions at high temperature, the presence of H_2O and SO_2 can also reduce the oxidation of NH_3 to NO in homogeneous reaction which is mentioned before in Figure 4.20.
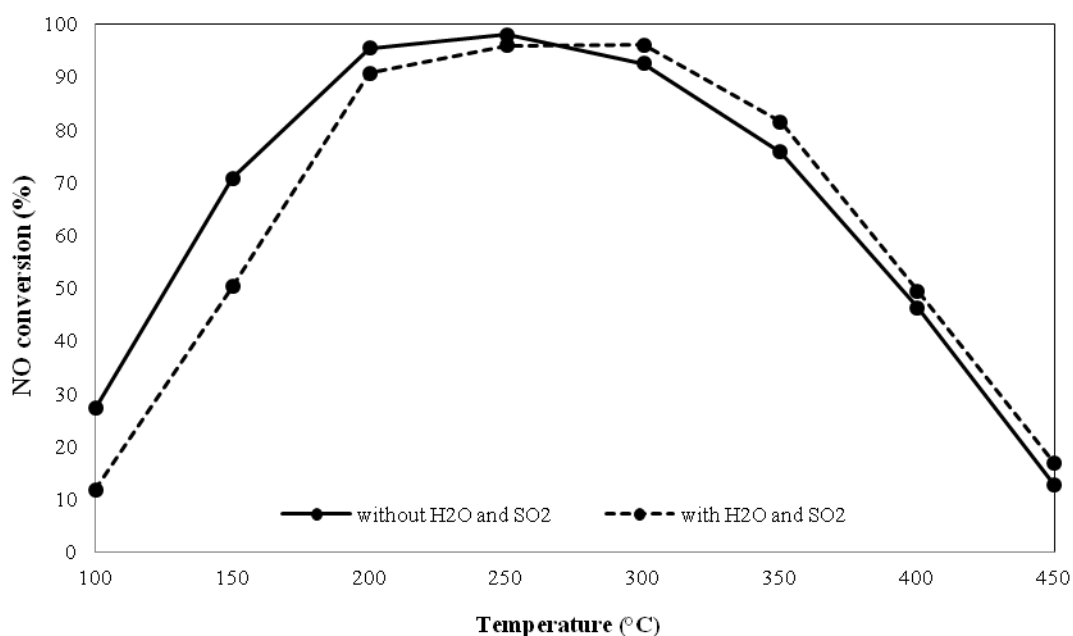

Figure 4.21 The SCR activity over 3V7W10Mo#2/TiO_2 catalyst.
Reaction conditions: [NH_3] = [NO] = 120 ppm, [O_2] = 15%, [SO_2] = 30 ppm,
[H_2O] = 15%, N_2 balance and WHSV = 120,000 ml/g-h.

- 3V7W10Mo#3:

The result in Figure 4.22 indicates that when H_2O and SO_2 present in the feed gas, the NO conversion-reaction temperatures profiles obtained from the first run and the second run are different significantly due to the effect of H_2O and SO_2. The effects of H_2O and SO_2 on the $DeNO_x$ activity of this catalyst are the same as of 3V7W10Mo#2. At low temperature the NO conversions are significantly lower when H_2O and SO_2 present in the feed gas. In addition, at high temperature the NO conversions are higher than without H_2O and SO_2. The reason for this behavior is the competitive adsorption of H_2O and SO_2 as described previously in the previous paragraph. The benefit of H_2O and SO_2 in this catalyst, however, is less than in the previous catalyst, 3V7W10Mo#2.
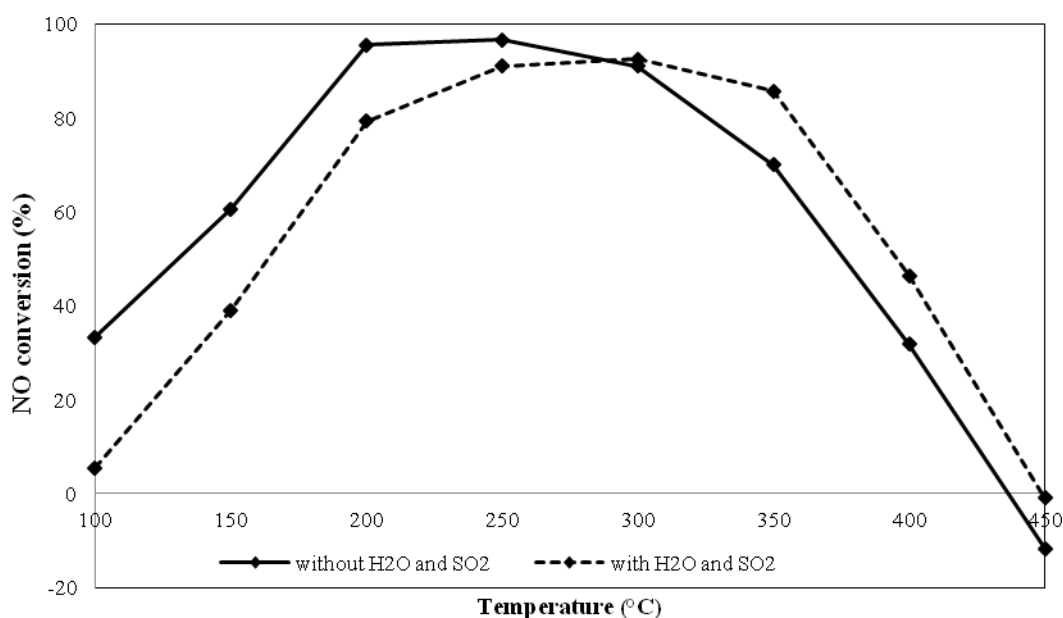

Figure 4.22 The SCR activity over 3V7W10Mo#3/TiO_2 catalyst.
Reaction conditions: $[NH_3] = [NO] = 120$ ppm, $[O_2] = 15\%$, $[SO_2] = 30$ ppm,
$[H_2O] = 15\%$, N_2 balance and WHSV = 120,000 ml/g-h.

The comparison of the two selected catalysts at the same feed gas compositions are plotted altogether in Figure 4.23. The results indicate that at high temperature 300 ℃, 3V7W10Mo#2 has higher SCR activity than 3V7W10Mo#3. In addition, the results show that at this temperature, 3V7W10Mo#2 causes the oxidation of NH_3 less than 3V7W10Mo#3. Therefore, from the above experimental results the catalyst that shows optimal activity for the SCR is selected for further studies is 3V7W10Mo#2.
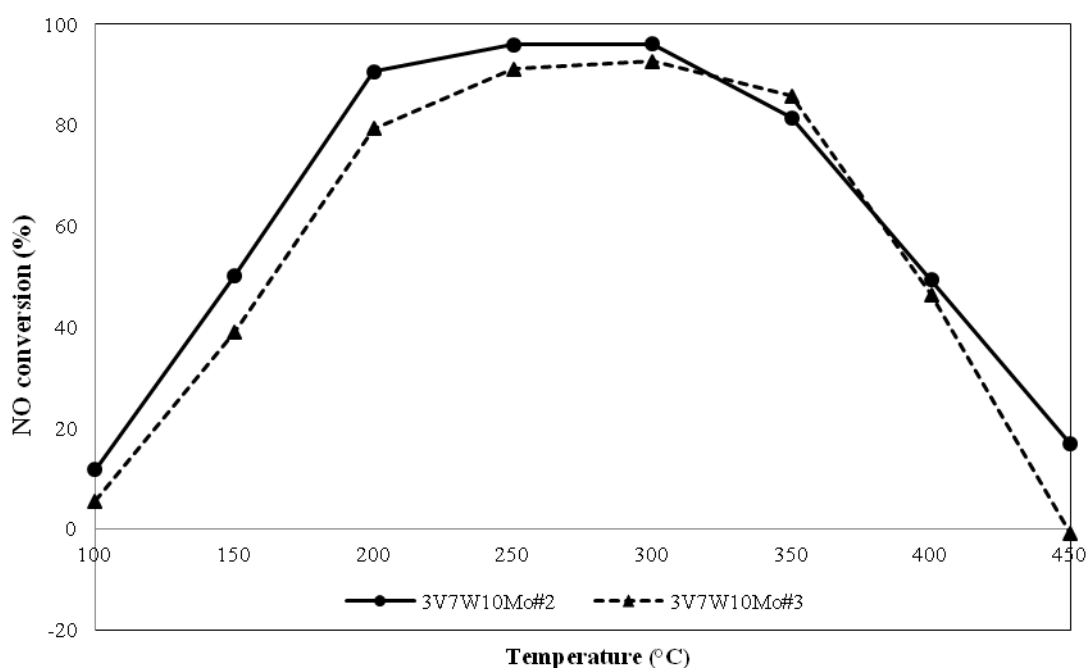

Figure 4.23 The SCR activity over 3V7W10Mo#2/TiO$_2$ and 3V7W10Mo#3/TiO$_2$ catalysts. Reaction conditions: [NH$_3$] = [NO] = 120 ppm, [O$_2$] = 15%, [SO$_2$] = 30 ppm, [H$_2$O] = 15%, N$_2$ balance and WHSV = 120,000 ml/g-h.

4.2.3 Effect of W and Mo loading on the activity of V_2O_5-WO_3-MoO_3/TiO_2

From the above mentioned in the previous section 4.2.2, the 3V7W10Mo#2 is selected in order to study the effect of varying composition of W and Mo. In this section, the activity of 3V7W10Mo#2, 3V7W5Mo#2, 3V3.5W10Mo#2 and 3V3.5W5Mo#2 catalysts are investigated in the presence of H_2O and SO_2 in the feed gas. The results of SCR activity over V_2O_5-WO_3-MoO_3/TiO_2 catalysts having various catalyst compositions in the reaction temperature range of 100-450°C and the NO concentrations from the NH_3 oxidation are shown in Figure 4.24-4.30. All catalysts are prepared by following the procedures given in section 3.1.5. These catalysts are calcined, at 500°C for 2 hours, 3 times (after adding V, after adding Mo and finally after adding W). The gas chromatograph Shimadzu GC-2014 equipped with a pulsed discharge detector (PDD) is used to measure NH_3 concentration in the effluent gas and convert to NO conversion.

- The Effect of decreasing Mo content

In this part, the two compositions of catalysts that remains the amount of W and changes the Mo composition are compared. The first profile is the SCR activity over 3V7W10Mo#2 catalyst. The another is the profile of 3V7W5Mo#2.

The results in Figure 4.24 show that the overall effect of decreasing Mo from 3V7W10Mo#2 to 3V7W5Mo#2 is the decreasing of the NO conversion with the decrease of the content of Mo down to 5 wt.% MoO_3. From Figure 4.25, the NO concentration from the oxidation of NH_3 over 3V7W10Mo#2 and 3V7W5Mo#2 catalysts indicate that 3V7W5Mo#2 causes the NH_3 oxidation more than 3V7W10Mo#2. Therefore, this effect hardly enhances the SCR activity.
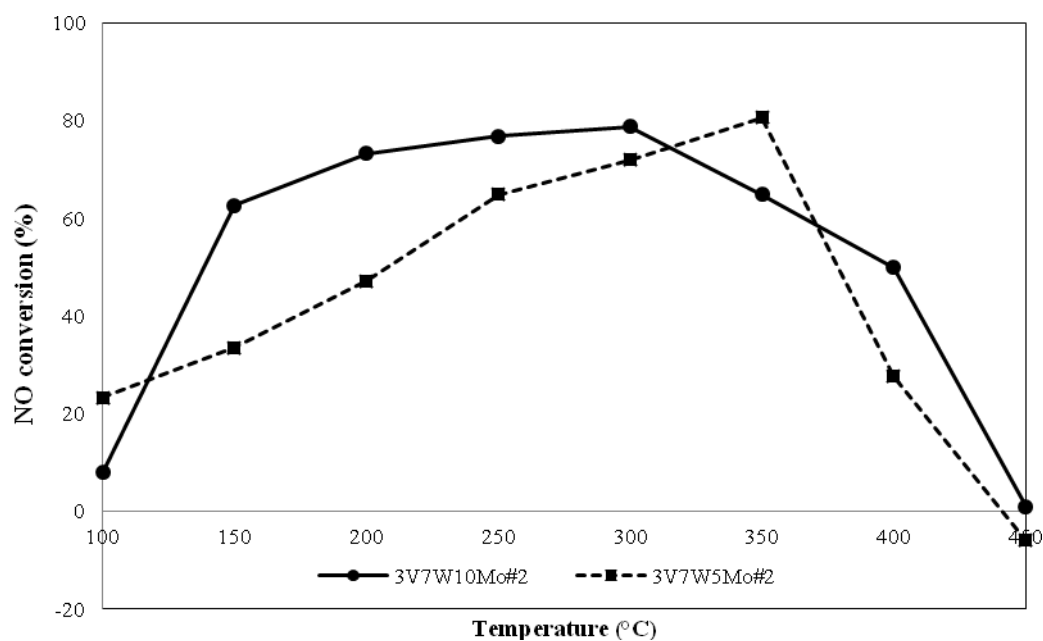
Figure 4.24 The SCR activity over 3V7W10Mo#2/TiO$_2$ and 3V7W5Mo#2/TiO$_2$ catalysts. Reaction conditions: [NH$_3$] = [NO] = 120 ppm, [O$_2$] = 15%, [SO$_2$] = 30 ppm, [H$_2$O] = 15%, N$_2$ balance and WHSV = 120,000 ml/g-h.
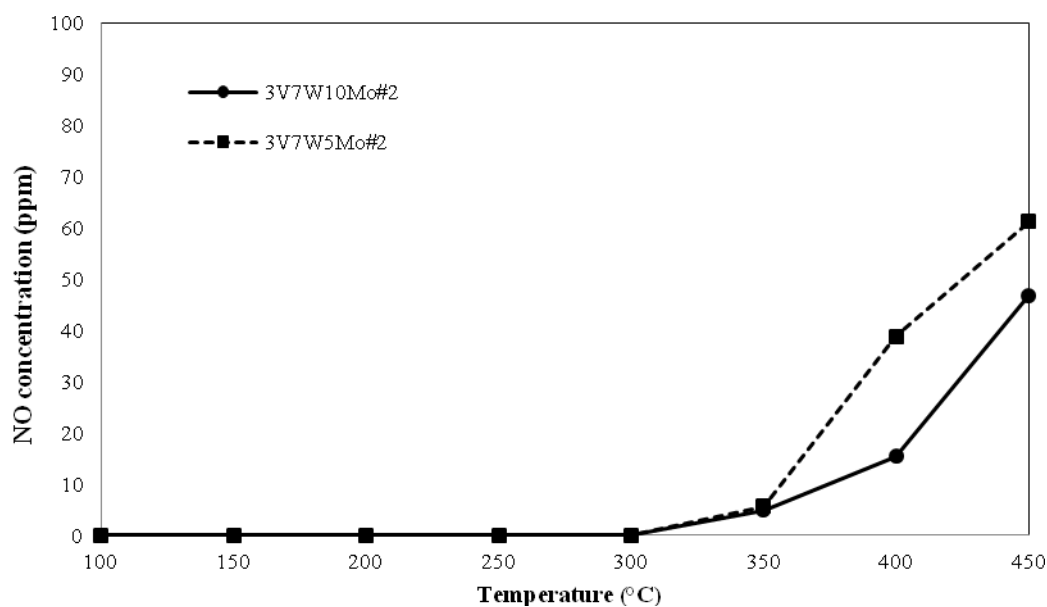

Figure 4.25 The NO concentration from the oxidation of NH$_3$ over 3V7W10Mo#2/TiO$_2$ and 3V7W5Mo#2/TiO$_2$ catalysts. Reaction conditions: [NH$_3$] = 120 ppm, [O$_2$] = 15%, [SO$_2$] = 30 ppm, [H$_2$O] = 15%, N$_2$ balance and WHSV = 120,000 ml/g-h.

- The Effect of decreasing W content

This part is the comparison between 3V7W10Mo#2 and 3V3.5W10Mo#2 by changing W and remaining Mo compositions.

The results from Figure 4.26 indicate that the overall effect of decreasing W from 3V7W10Mo#2 to 3V3.5W10Mo#2 is the decreasing of the SCR activity with the decrease of the content down of W to 3.5 wt.% WO_3. In addition, the NO concentration from the oxidation of NH_3 over 3V7W10Mo#2 and 3V3.5W10Mo#2 catalysts from Figure 4.27 show that this effect causes the NH_3 oxidation more than 3V7W10Mo#2 as the previous effect, decreasing Mo.
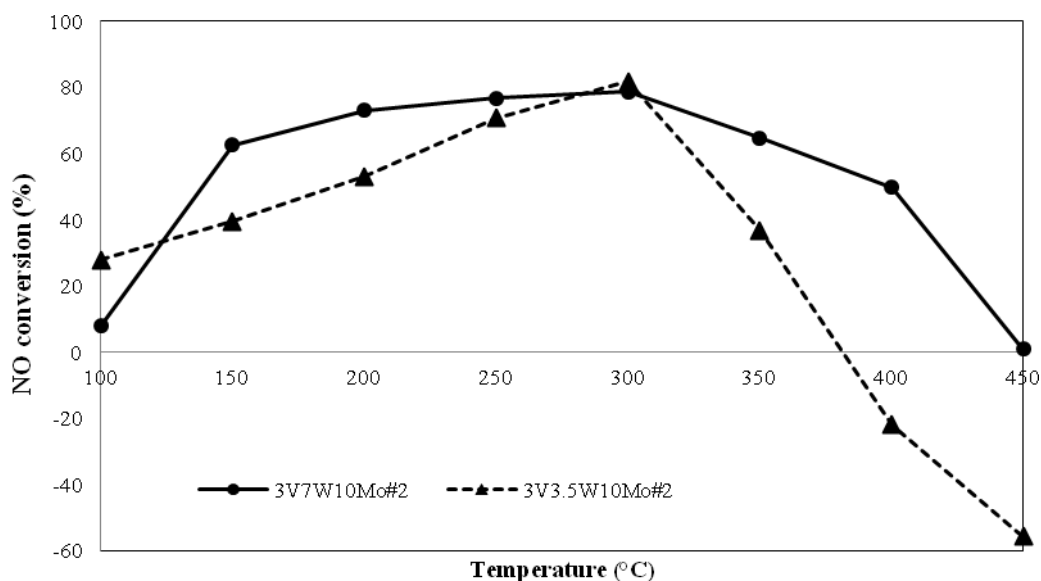

Figure 4.26 The SCR activity over 3V7W10Mo#2/TiO_2 and 3V3.5W10Mo#2/TiO_2 catalysts. Reaction conditions: [NH_3] = [NO] = 120 ppm, [O_2] = 15%, [SO_2] = 30 ppm, [H_2O] = 15%, N_2 balance and WHSV = 120,000 ml/g-h.
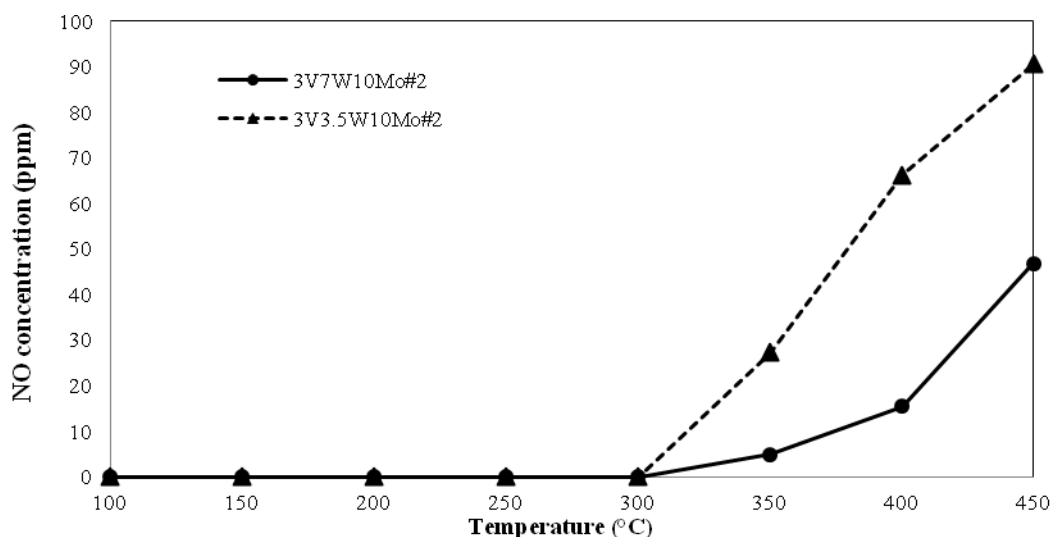
Figure 4.27 The NO concentration from the oxidation of NH_3 over 3V7W10Mo#2/TiO_2 and 3V3.5W10Mo#2/TiO_2 catalysts. Reaction conditions: $[NH_3]$ = 120 ppm, $[O_2]$ = 15%, $[SO_2]$ = 30 ppm, $[H_2O]$ = 15%, N_2 balance and WHSV = 120,000 ml/g-h.

- The Effect of decreasing both W and Mo content

In this part, the two compositions of catalysts that 3V7W10Mo#2 and 3V3.5W5Mo#2 by changing both W and Mo compositions, are compared.

The results from Figure 4.28 show that the effect of decreasing W and Mo from 3V7W10Mo#2 to 3V3.5W5Mo#2 slightly decreases the SCR activity at low temperature. Moreover, from Figure 4.29, this effect causes the increasing NH_3 oxidation reaction significantly.
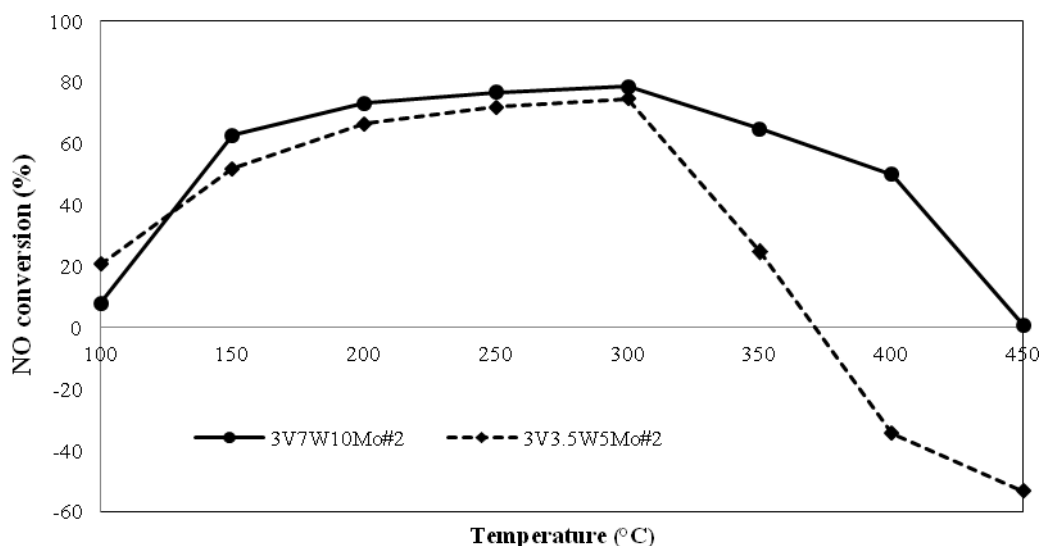
Figure 4.28 The SCR activity over 3V7W10Mo#2/TiO$_2$ and 3V3.5W5Mo#2/TiO$_2$ catalysts. Reaction conditions: [NH$_3$] = [NO] = 120 ppm, [O$_2$] = 15%, [SO$_2$] = 30 ppm, [H$_2$O] = 15%, N$_2$ balance and WHSV = 120,000 ml/g-h.
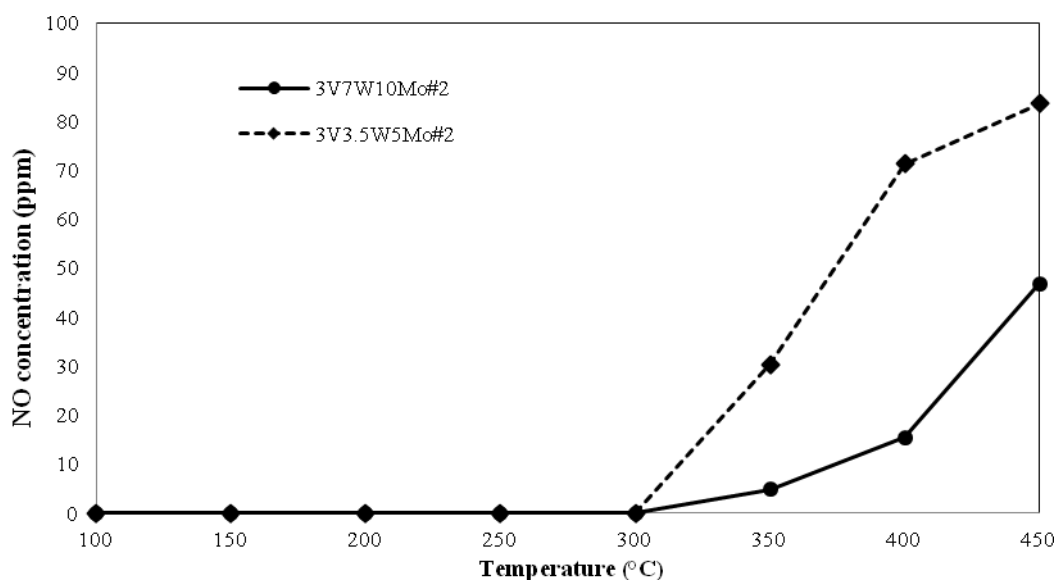

Figure 4.29 The NO concentration from the oxidation of NH$_3$ over 3V7W10Mo#2/TiO$_2$ and 3V3.5W5Mo#2/TiO$_2$ catalysts. Reaction conditions: [NH$_3$] = 120 ppm, [O$_2$] = 15%, [SO$_2$] = 30 ppm, [H$_2$O] = 15%, N$_2$ balance and WHSV = 120,000 ml/g-h.

The four profiles showed in Figures 4.24, 4.26 and 4.28 are plotted altogether in Figure 4.30. The results indicates that the presence of W is necessary to prevent the oxidation of NH_3 at reaction temperature higher than 300°C.

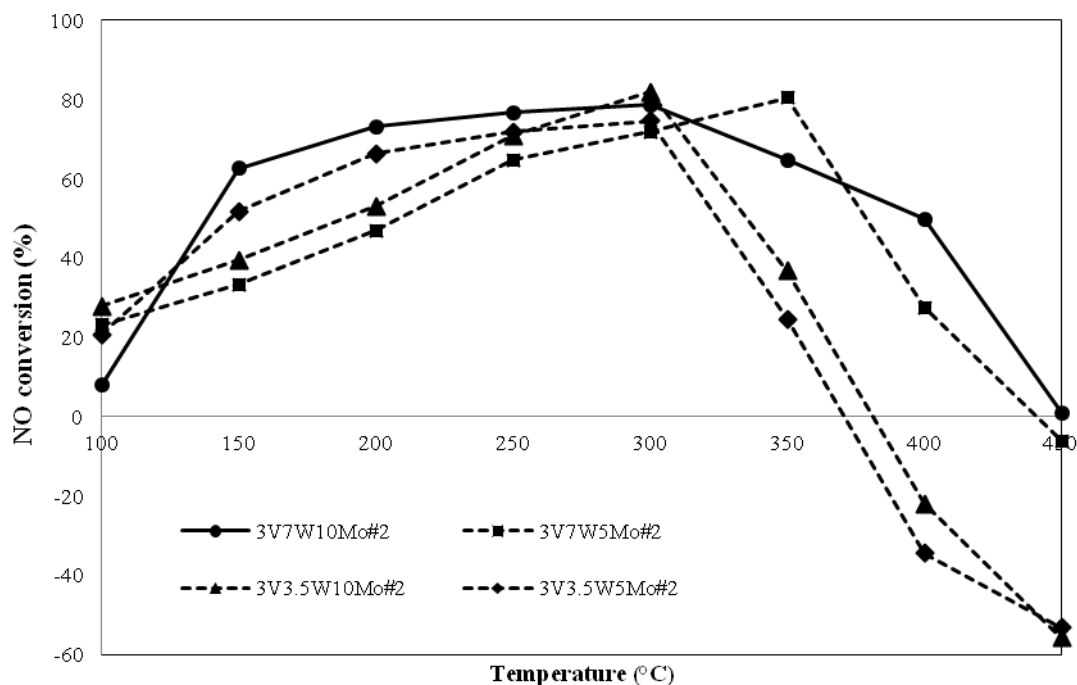**Figure 4.30** The SCR activity over V_2O_5-WO_3-MoO_3/TiO_2 catalysts having various catalyst compositions. Reaction conditions: $[NH_3] = [NO] = 120$ ppm, $[O_2] = 15\%$, $[SO_2] = 30$ ppm, $[H_2O] = 15\%$, N_2 balance and WHSV = 120,000 ml/g-h.

4.2.4 Comparison of the activity of V_2O_5-WO_3/TiO_2, V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3-MoO_3/TiO_2

The catalytic performances of V_2O_5-WO_3-MoO_3/TiO_2 catalyst for SCR reaction compared with V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 catalyst are shown in Figure 4.31. In this section the activity of all catalysts are investigated in the presence of H_2O and SO_2 in the feed gas. NO_x analyzer Shimadzu NOA-7000 is used to measure NO concentration in the effluent gas.

The results of 3V7W/TiO_2 is brought from the our previous research of Kaewbuddee, 2010. The results of 3V10Mo/TiO_2 is brought from the previous work of Taweesuk, 2011. The result of 3V7W10Mo/TiO_2 is obtained from the present work which is the continuation of the works of Kaewbuddee, 2010 and Taweesuk, 2011.

From Figure 4.30, the NO conversion of 3V7W10Mo#2 is higher than 3V7W and 3V10Mo at low and intermediate temperature region. But at high temperature 3V7W and 3V10Mo gives higher NO conversion than 3V7W10Mo#2. In addition, at the high temperature, causes the oxidation of NH_3 more than the other catalysts. However, 3V7W10Mo#2 is the catalyst that has the higher stability and repeatability. The presence of H_2O and SO_2 hardly effects to this catalyst stability.

The results show that the combination of W and Mo on V_2O_5/TiO_2 SCR catalyst can yield a catalyst to operate in the low and intermediate temperature region (150-300°C).

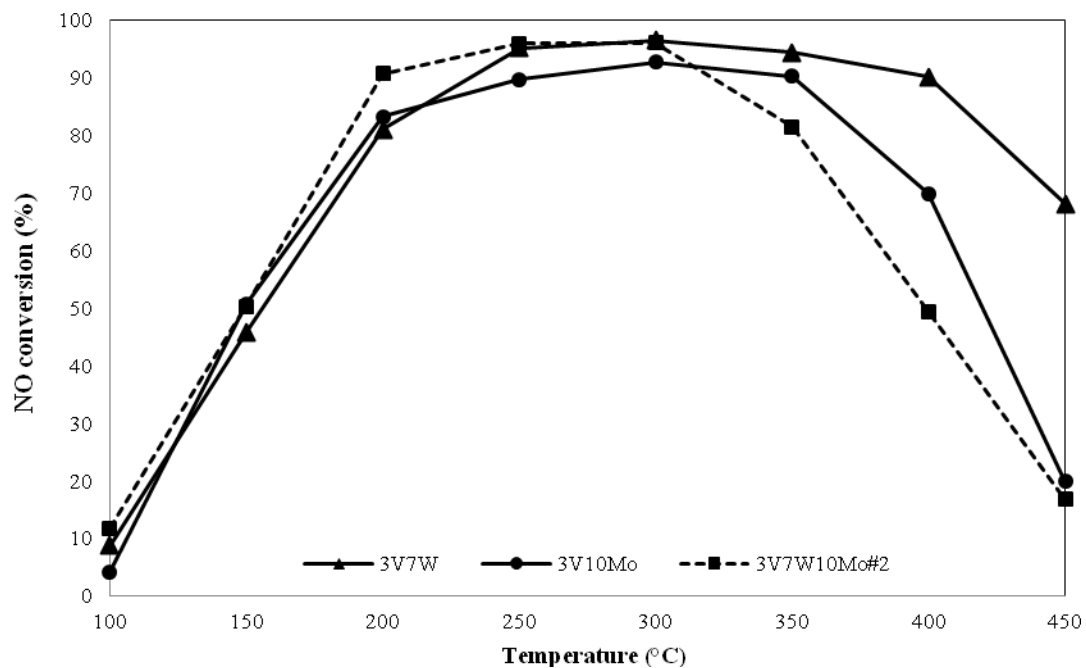**Figure 4.31** Comparison of the activity of V_2O_5-WO_3/TiO_2, V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3-MoO_3/TiO_2. Reaction conditions: [NO] = [NH_3] =120 ppm, [O2] = 15%, [SO_2] = 30 ppm, [H_2O] = 15%, N_2 balance, WHSV = 120,000 ml/g-h.

Conclusions

From the all experiment results that discussed in this chapter, the conclusions are following:

- The suitable method of loading metal oxides sequences on the support and calcination sequences to form oxide compounds in this work is the preparation of WO_3 and MoO_3 over V_2O_5/TiO_2 catalyst Method II in the section 3.1.5.

- The suitable composition of WO_3 and MoO_3 over V_2O_5/TiO_2 catalyst is 7 and 10 wt.% respectively, 3V7W10Mo catalyst.

- It should be kept in mind that this work does not attempt to find the best catalyst but to find a suitable catalyst for a specific operating condition. Therefore, the V_2O_5-WO_3-MoO_3/TiO_2 system, especially 3V7W10Mo#2, proper to operate in the low and intermediate temperature region (150-300°C). Therefore, this catalyst can allow the power plant to recover more heat from the flue gas before entering the DeNOx system.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 5.1 provides the conclusions obtained from the experimental results. Additionally, recommendations for further study are given in section 5.2.

5.1 Conclusions

- Loading metal oxides sequences on the support and calcination sequences influence the SCR activity and the catalyst stability significantly, the selected catalyst for further varying composition is 3V7W10Mo prepared by Method II which is calcined, at 500°C for 2 hours, 3 times (after adding V, after adding Mo and finally after adding W).

- The suitable composition of WO_3 and MoO_3 over V_2O_5/TiO_2 catalyst is 7 and 10 wt.% respectively, 3V7W10Mo catalyst. In addition, the decreasing of the content of W and Mo down from 7 and 10 wt.% respectively by changing the compositions does not improve the SCR activity.

- The oxidation of NH_3 to NO can occur at temperature above 300 ºC and the presence of H_2O and SO_2 can reduce the oxidation of NH_3 to NO. The H_2O and SO_2 block site position of NH_3 oxidation in order to occur lower NH_3 oxidation reaction.

- This research determine the optimal catalyst for various conditions, did not the best catalyst. As a result, each operating condition is suitable for different catalyst. The 3VxWyMo catalysts system present good catalytic performances at low to intermediate temperature region, while 3V10Mo gives higher NO conversion than 3VxWyMo catalyst system at intermediate to high temperature. For the catalyst shows good catalytic performances at high temperature (above 250ºC) and gives high NO conversion in wide reaction temperature range is 3V7W catalyst.

5.2 Recommendations

       - The poisoning of sulfur component, SO_2 and SO_3, on the catalysts should be further investigated.

       - In the oxidation reaction, NH_3 reacts with oxygen rather than NO to form nitrogen oxides. N_2O may occur from this reaction. Therefore, N_2O should be further investigated for further research.

       - For the catalyst preparation, the loading metal oxides sequences effect to SCR activity. Therefore, we should load Mo before W over V_2O_5/TiO_2. From the reason of V and Mo can form the composite oxide after calcinations (Tachi et al., 1990). If we load W before Mo, WO_3 may hidden the formation of V-Mo-O. In addition, the FT-IR spectra show the occurrence of V and Mo composite oxide of the catalyst that prepare by loading Mo before W over V_2O_5/TiO_2 significantly.

REFERENCES

Beretta A., Orsenigo G., Ferlazzo N., Tronconi E. and Forzatti P. Analysis of the performance of plate-type monolithic catalysts for selective catalytic reduction deNOx applications. Ind. Eng. Chem. Res. 37 (1998): 2623-2633.

Boudali L. K., Ghorbel A. and Grange P. Characterization and reactivity of WO_3-V_2O_5 supported on sulfated titanium pillared clay catalysts for the SCR-NO reaction. C. R. Chimie 12 (2009): 1-8.

Busca G., Liettib L., Ramisa G. and Bertic F. Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review. Applied Catalysis B: Environmental 18 (1998): 1-36.

Casagrande L., Lietti L., Nova I., Forzatti P. and Baiker A. SCR of NO by NH_3 over TiO_2-supported V_2O_5–MoO_3 catalysts: reactivity and redox behavior. Applied Catalysis B: Environmental 22 (1999): 63–77.

Chen J.P. and Yang R.T. Role of WO_3 in mixed V_2O_5-WO_3/TiO_2 catalysts for selective catalytic reduction of nitric oxide with ammonia. Applied Catalysis A, General 80 (1992):135-148.

Dierad S., Tifouti L., Crocoll M. and Weisweiler W. Effect of vanadia and tungsten loadings on the physical and chemical characteristics of V_2O_5-WO_3/TiO_2 catalysts. Journal of Molecular Catalysis A: Chemical 208 (2004): 257–265.

Djerad S., Crocoll M., Kureti S., Tifouti L. and Weisweiler W. Effect of oxygen concentration on the NO_X reduction with ammonia over V_2O_5–WO_3/TiO_2 catalyst. Catalysis Today 113 (2006): 208–214.

Forzatti P. Environmental catalysis for stationary applications. Catalysis Today 62 (2000): 51–65.

Huang Z., Zhu Z. and Liu Z. Combined effect of H_2O and SO_2 on V_2O_5/AC catalysts for NO reduction with ammonia at lower temperatures. Applied Catalysis B: Environmental 39 (2002): 361–368.

Jung S. M. and Grange P., DRIFTS investigation of V=O behavior and its relations with the reactivity of ammonia oxidation and selective catalytic reduction of NO over V_2O_5 catalyst. Applied Catalysis B: Environmental 36 (2002): 325–332.

Kaewbuddee C. Selective catalytic reduction (SCR) of nitrogen oxide by ammonia over V_2O_5-WO_3/TiO_2 catalysts. Mater's Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn university 2009.

Kamata H., Ohara H., Takahashi K., Yukimura A. and Seo Y. SO_2 oxidation over the V_2O_5/TiO_2 SCR catalyst. Catalysis Letters 73 (2001): 79-83.

Kleemann M., Elsener M., Koebel M. and Wokaun A. Investigation of the ammonia adsorption on monolithic SCR catalysts by transient response analysis. Applied Catalysis B: Environmental 27 (2000): 231–242.

Lietti L., Nova I. and Forzatti P. Selective catalytic reduction (SCR) of NO by NH_3 over TiO_2-supported V_2O_5–WO_3 and V_2O_5–MoO_3 catalysts. Topics in Catalysis 11/12 (2000): 111–122.

Lin C. and Bai H. Surface acidity over vanadia/titania catalyst in the selective catalytic reduction for NO removal-in situ DRIFTS study. Applied Catalysis B: Environmental 42 (2003): 279–287.

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

Nova I., Liettia L.,Casagrandea L., Dall'Acquab L., Giamellob E. and Forzatti P. Characterization and reactivity of TiO_2-supported MoO_3 De-NO_x SCR catalysts. Applied Catalysis B: Environmental 17 (1998): 245-258.

Nova I., Lietti L., Tronconi E. and Forzatti P. Dynamics of SCR reaction over a TiO_2-supported vanadia–tungsta commercial catalyst. Catalysis Today 60 (2000): 73–82.

Oh H.K. Selective catalytic reduction (SCR) of nitric oxide (NO) with ammonia over vanadia-based and pillared interlayer clay-based catalyst. Master's Thesis, Texas A&M University, 2004.

Orsenigo C., Lietti L., Tronconi E., Forzatti P. and Bregani F. Dynamic investigation of the role of the surface sulfates in NO_X reduction and SO_2 oxidation over V_2O_5-WO_3/TiO_2 catalysts. Ind. Eng. Chem. Res. 37 (1998): 2350-2359.

Paganini M.C., Dall'Acqua L., Giamello E., Lietti L., Forzatti P. and Busca G. An EPR study of the surface chemistry of the V_2O_5–WO_3/TiO_2 catalyst: Redox behaviour and state of V(IV). Journal of Catalysis 166 (1997): 195–205.

Park T.S., Jeong S.K., Hong S.H. and Hong S.C. Selective catalytic reduction of nitrogen oxides with NH_3 over natural manganese ore at low temperature. Ind. Eng. Chem. Res. 40 (2001): 4491-4495.

Qi G. and Yang R.T. Low-temperature selective catalytic reduction of NO with NH_3 over iron and manganese oxides supported on titania. Applied Catalysis B: Environmental 44 (2003): 217–225.

Reiche M. A., Hug P. and Baiker A. Effect of grafting sequence on the behavior of titania-supported V_2O_5-WO_3 catalysts in the selective reduction of NO by NH_3. Journal of Catalysis 192 (2000): 400-411.

Tachi T., Kato A., Kawagoshi H., Yamashita H., Kamo T. and all of Hitachi Japan. United States Patent, Patent Number: 4,925,825 (1990).

Tang X., Hao J., Xu W. and Li J. Low temperature selective catalytic reduction of NO_X with NH_3 over amorphous MnO_X catalysts prepared by three methods. Catalyst Communication 8 (2007): 329-334.

Taweesuk B. Selective catalytic reduction (SCR) of nitrogen oxide by ammonia over V_2O_5-MoO_3/TiO_2 catalysts. Mater's Thesis, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn university 2011.

APPENDICES

APPENDIX A

CALIBRATING DATA FOR MASS FLOW METER, NO$_X$ ANALYZER AND GC 2014

A1 Calibration data of mass flow meter are shown as follows:

Component of feed gas mixture: ammonia, nitrogen oxide, nitrogen, oxygen and sulfur dioxide

A1.1 Calibration for ammonia mass flow controller

Use the bubble flow by passing the gas through the glass tube in order to measure the time. Record the time from scale 0 ml to 5 ml of tube.

Table A1 Calibration data of ammonia mass flow controller.

| Mass flow meter scale (ml/min)	Time (sec)			Time average (sec)	Actual flow (ml/min)
	#1	#2	#3		
1	54.62	54.91	55.91	55.15	2.18
2	25.03	24.91	24.88	24.94	4.81
3	16.09	15.69	15.84	15.87	7.56
4	11.97	11.84	11.87	11.89	10.09
5	9.38	9.47	9.38	9.41	12.75
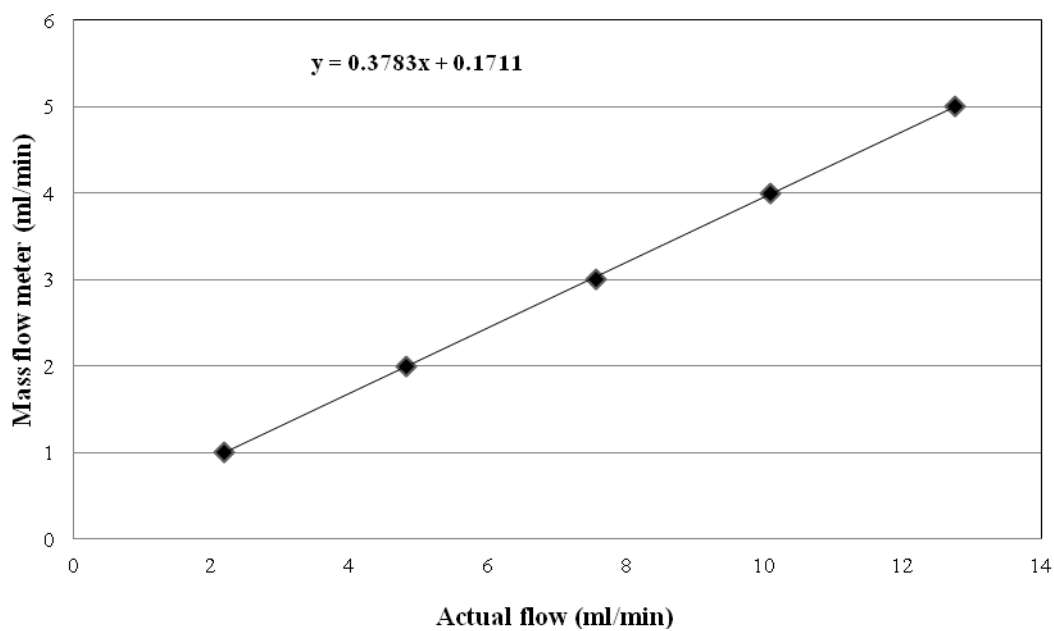
Figure A1 Calibration curve of ammonia mass flow controller.

A1.2 Calibration for nitrogen oxide mass flow controller

Use the bubble flow by passing the gas through the glass tube in order to measure the time. Record the time from scale 0 ml to 5 ml of tube.

Table A2 Calibration data of nitrogen oxide mass flow controller.

| Mass flow meter (ml/min)	Time (sec)			Time average (sec)	Actual flow (ml/min)
	#1	#2	#3		
1	75.38	80.25	75.97	77.20	1.43
2	34.22	35.00	37.75	35.66	3.09
3	22.82	23.78	23.37	23.32	4.73
4	17.50	17.37	18.04	17.64	6.37
5	13.78	13.47	14.16	13.80	7.81
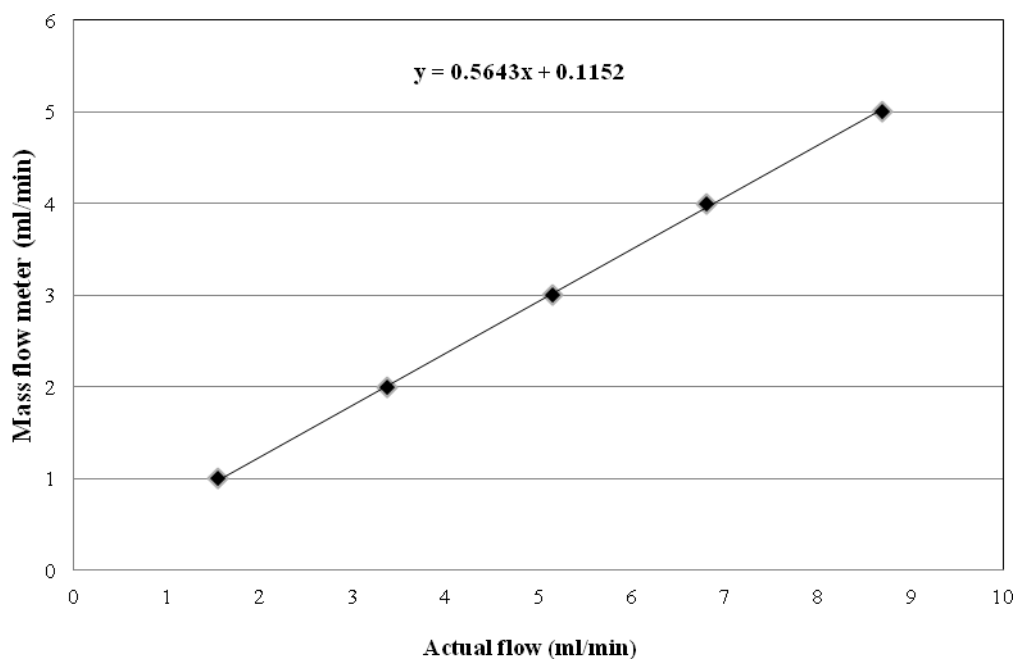
Figure A2 Calibration curve of nitrogen oxide mass flow controller.

A1.3 Calibration for oxygen mass flow controller

Use the bubble flow by passing the gas through the glass tube in order to measure the time. Record the time from scale 0 ml to 5 ml of tube.

Table A3 Calibration data of oxygen mass flow controller.

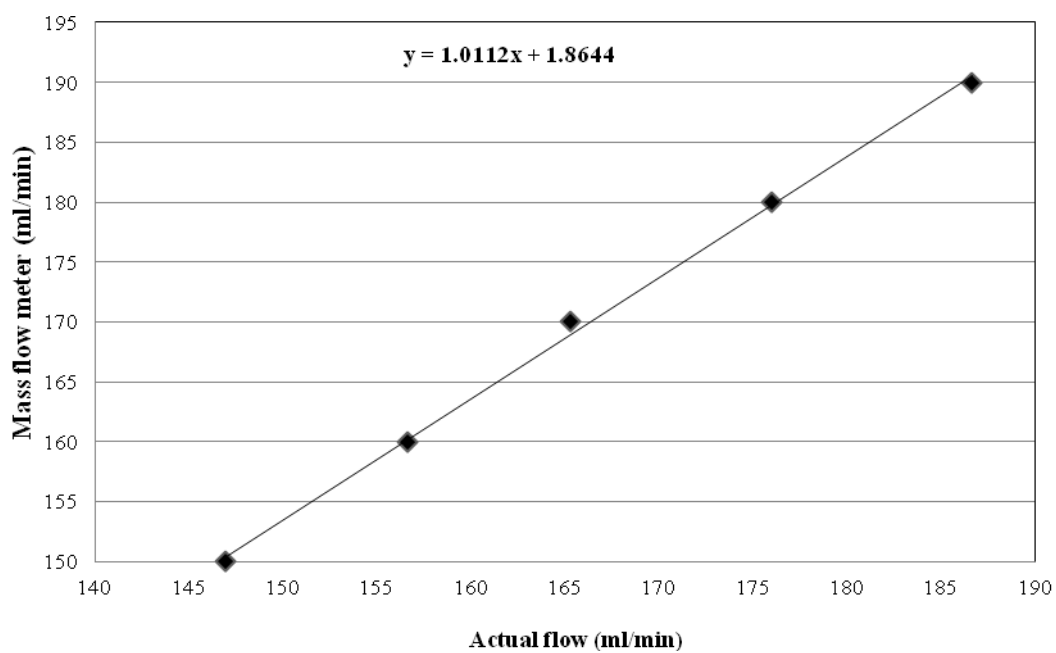| Mass flow meter (ml/min)	Time (sec)			Time average (sec)	Actual flow (ml/min)
	#1	#2	#3		
10	55.56	55.50	55.44	55.50	10.81
20	28.00	27.97	28.00	27.99	21.44
30	18.85	18.75	18.44	18.68	32.12
40	14.07	14.10	14.03	14.07	42.65
50	11.13	11.18	11.25	11.19	53.64
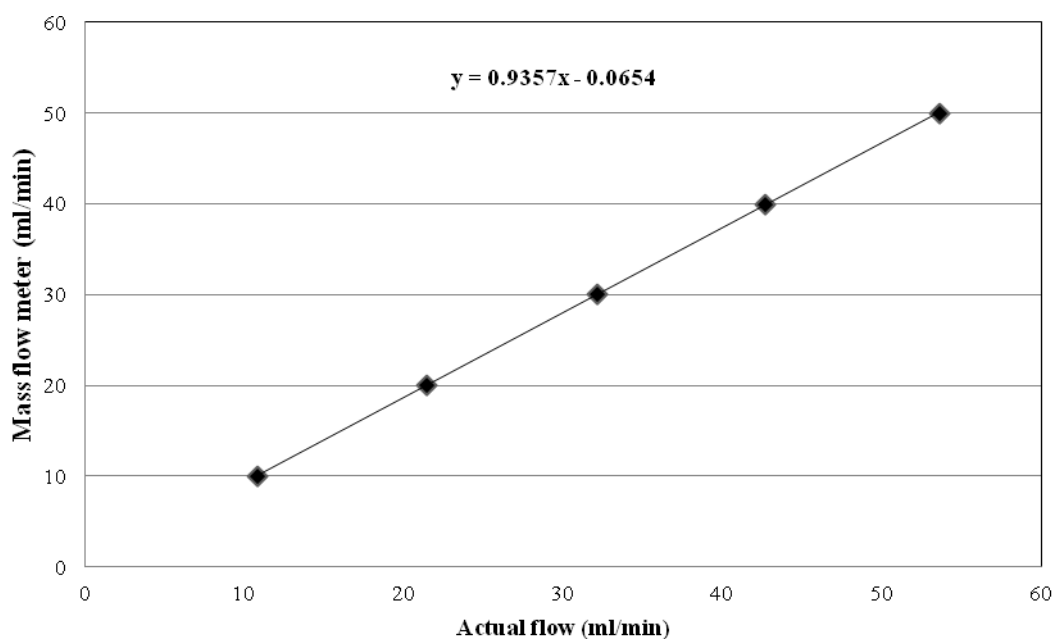
Figure A3 Calibration curve of oxygen mass flow controller.

A1.4 Calibration for nitrogen mass flow controller

Use the bubble flow by passing the gas through the glass tube in order to measure the time. Record the time from scale 0 ml to 5 ml of tube.

Table A4 Calibration data of nitrogen mass flow controller.

Mass flow meter (ml/min)	Time (sec)			Time average (sec)	Actual flow (ml/min)
	#1	#2	#3		
150	8	8	8	8	147
160	8	8	8	8	157
170	7	7	7	7	165
180	7	7	7	7	176
190	7	6	6	6	187

Figure A4 Calibration curve of nitrogen mass flow controller.

A1.5 Calibration for sulfur dioxide mass flow controller

Use the bubble flow by passing the gas through the glass tube in order to measure the time. Record the time from scale 0 ml to 5 ml of tube.

Table A5 Calibration data of sulfur dioxide mass flow controller.

Mass flow meter (ml/min)	Time (sec)			Time average (sec)	Actual flow (ml/min)
	#1	#2	#3		
1	84.9	82.5	83.59	83.66	1.43
2	38.72	38.65	39.06	38.81	3.09
3	25.34	25.50	25.31	25.38	4.73
4	18.75	18.84	18.94	18.84	6.37
5	15.32	15.43	15.37	15.37	7.81
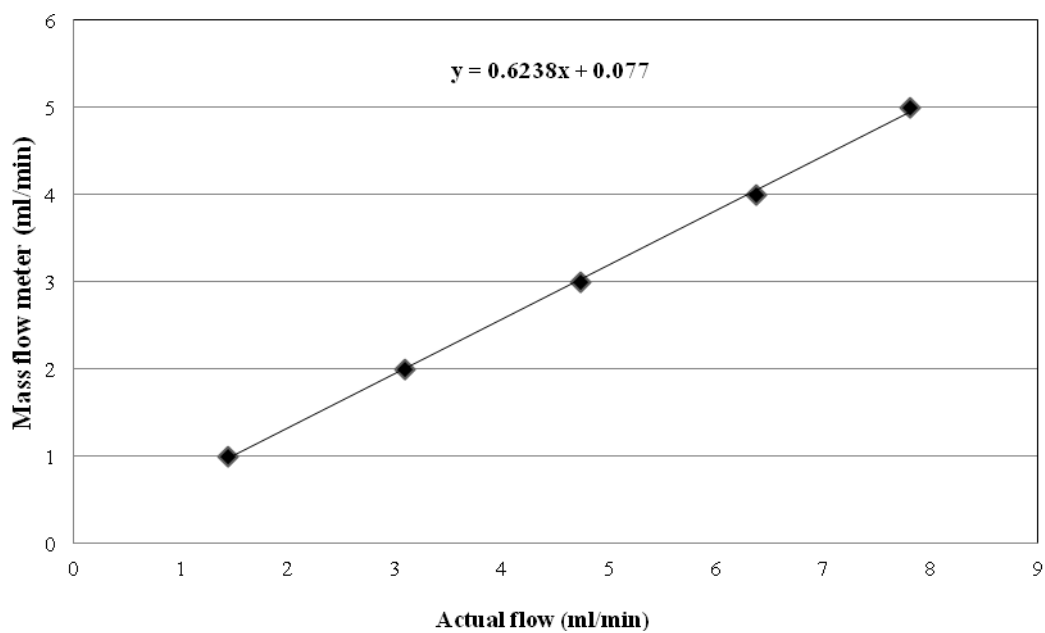
Figure A5 Calibration curve of sulfur dioxide mass flow controller.

A2 Calculation and Calibration of NO_X analyzer is shown as follows:

The example calculation used the following conditions: 120 ppm NH_3, 120 ppm NO, 15% O_2, balanced N_2 (The flow of mix gas = 200 ml/min) and add air at the point before measure in NO_X analyzer (The flow of air 1250 ml/min)

Total flow = 1250 + 200 = 1450 ml/min
= 1450/200 = 7.25 times

It means that dilute gas 7.25 times. Therefore, the value on the screen of NO_X analyzer should be = 120/7.25 = 16.55 ppm. This is value for NO_X analyzer calibration.

Steps for measurement are as following:

When "Ready" is displayed on the monitor screen, set the NO concentration (NO concentration is diluted = 16.55 ppm) that we need to calibrate into NO_X analyzer. Press CAL bottom, then press to adjust the value and following by SPAN bottom. Wait for calibrating after that press MAES bottom to measure NO concentration.

Assume that if the NO concentration displayed on the monitor screen is 2 ppm. Therefore it is indicated that actual NO concentration is = 2 × 7.25 = 14.5 ppm.

The NO conversion is evaluated following this equation.

$$\% \text{ NO conversion} = \frac{\text{NO conc. in feed} - \text{NO conc. in effluent gas}}{\text{NO conc. in feed}} \times 100 \qquad \text{(eq. A2)}$$

A3 Calculation and Calibration of GC 2014 PDD is shown as follows:

A3.1 NO concentration in the effluent gas is calculated as follows:

The value of NO concentration is measured by GC 2014 PDD in form of ammonia concentration at the effluent gas. The conversion of NO can be calculated using the following steps.

NH_3 converted $\quad\quad = \quad NH_3$ inlet - NH_3 outlet $\quad\quad\quad$ (eq. A3.1.1)

In the reaction having no NO (NH_3 oxidation reaction)

NH_3 oxidized by $O_2 \quad = \quad NH_3$ converted $\quad\quad\quad\quad\quad$ (eq. A3.1.2)

In the reaction having NO (SCR reaction)

NH_3 reacted with NO $\quad = \quad NH_3$ converted - NH_3 oxidized by $O_2 \quad$ (eq. A3.1.3)

Assume NH_3 and NO reacted ratio 1:1 molar ratio

NO in the effluent gas (NO_{out}) $\quad\quad = \quad NO_{in}$ - NH_3 reacted with NO
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ + NH_3 oxidized by $O_2 \quad\quad$ (eq. A3.1.4)

Therefore, $\quad$ % NO conversion $\quad = \quad \dfrac{NO_{in} - NO_{out}}{NO_{in}} \times 100 \quad\quad$ (eq. A3.1.5)

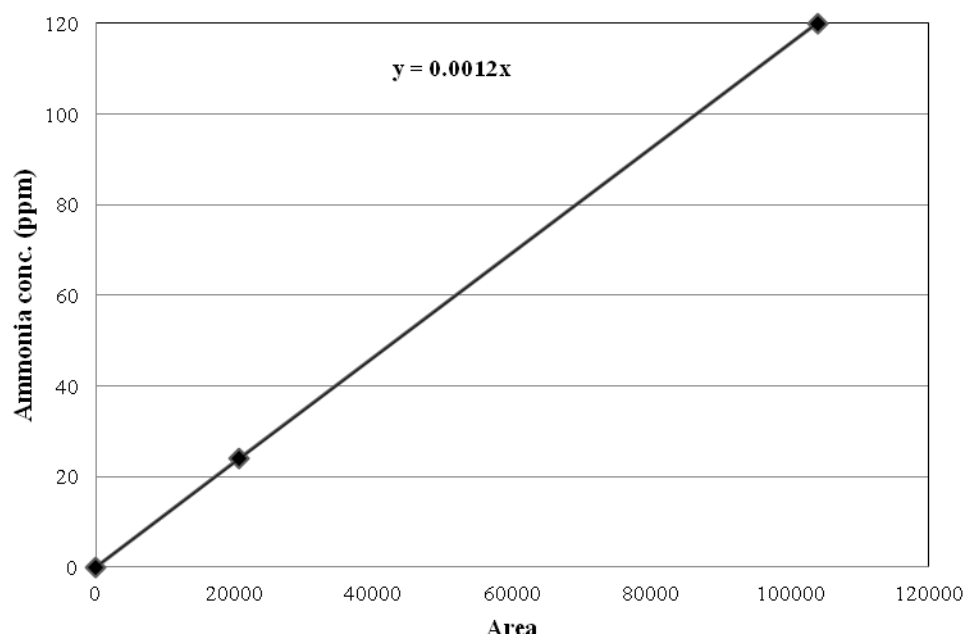A3.2 Calibration curve of GC 2014 PDD is shown as follows:

Figure A6 Calibration curve of GC 2014-PDD.

APPENDIX B

CALCULATION FOR CATALYST PREPARATION

Preparation of V_2O_5-WO_3-MoO_3/TiO_2 catalyst is shown as follows:

Reagent:

- Titania powder prepared by a sol-gel method

- Ammonium metavanadate 99.999%
  NH_4VO_3 (Aldrich)

- Ammonium metatungsteae hydrate 99.99%
  $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ (Aldrich)

- Ammonium heptamolybdate
  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Aldrich)

- Oxalic acid hydrate (Fluka)

Calculation for the preparation of V_2O_5-WO_3-MoO_3/TiO_2

Example calculation for the preparation of 3 wt. %V_2O_5-7 wt. %WO_3-10 wt. %MoO_3

Based on 2 g of catalyst used, the composition of the catalyst will be as follows:

V_2O_5	=	0.03×2	=	0.06 g
WO_3	=	0.07×2	=	0.14 g
MoO_3	=	0.06×2	=	0.12 g
TiO_2	=	2-0.06-0.14-0.12	=	1.60 g

Vanadium oxide 0.06 g was prepared from NH_4VO_3 and molecular weight of V_2O_5 is 180.39 g/mole.

$$NH_4VO_3 \text{ required} = \frac{\text{MW of } NH_4VO_3 \times \text{vanadium oxide required} \times 2}{\text{MW of } V_2O_5}$$

$$= \frac{116.98 \times 0.06 \times 2}{180.39} = 0.0778 \text{ g}$$

Tungsten oxide 0.14 g was prepared from $(NH_4)_6H_2W_{12}O_{40}\bullet xH_2O$ and molecular weight of WO_3 is 231.84 g/mole.

$$(NH_4)_6H_2W_{12}O_{40}\bullet xH_2O = \frac{(NH_4)_6H_2W_{12}O_{40}.xH_2O \times \text{tungsten oxide required}}{12 \times \text{MW of } WO_3}$$

$$= \frac{2956.3 \times 0.14}{231.84 \times 12} = 0.1488 \text{ g}$$

Molybdenum oxide 0.12 g was prepared from $(NH_4)MoO_4$ and molecular weight of MoO_3 is 143.94 g/mole

$$(NH_4)_2MoO_4 = \frac{(NH_4)_2MoO_4 \times \text{molybdenum oxide required}}{\text{MW of } MoO_3}$$

$$= \frac{196.02 \times 0.2}{143.94} = 0.2724 \text{ g}$$

Oxalic acid require

Mole of vanadium oxide   =   0.06/180.39   =   0.000333 mole

Molecular weight of oxalic acid equal to 126.07 g/mole.

Oxalic acid required   = 0.000333×126.07 =   0.0416 g

APPENDIX C

NH$_3$-TPD RAW DATA

The temperature-programmed desorption profiles for the V$_2$O$_5$-WO$_3$-MoO$_3$/TiO$_2$ catalysts are shown in Figures C1-C7. The amounts of acid sites and strong acid site are calculated from the area under the curve and are listed in Table C1.
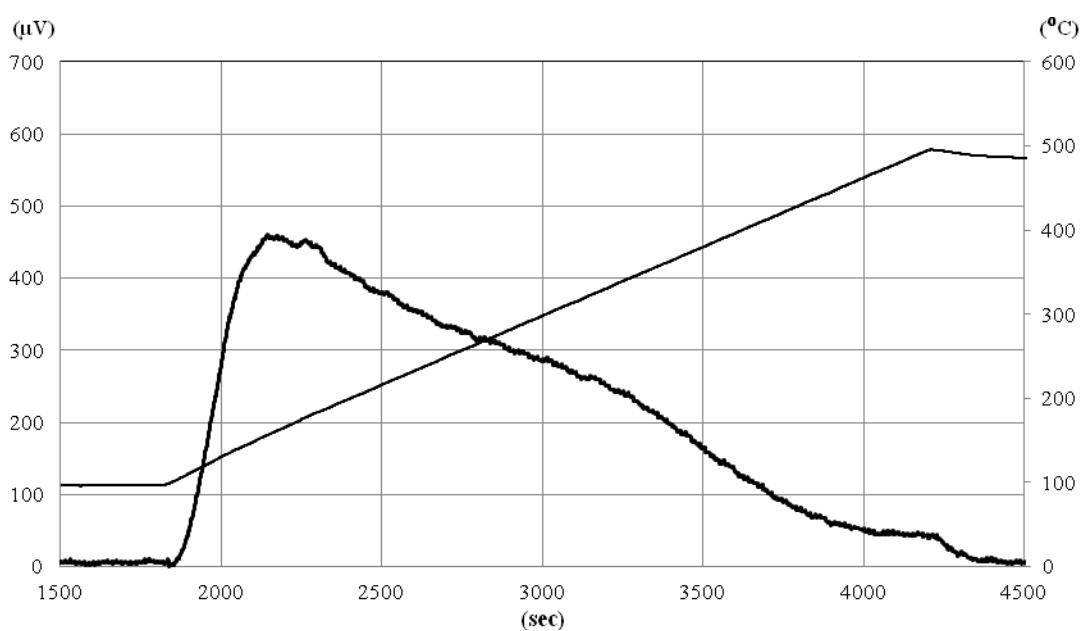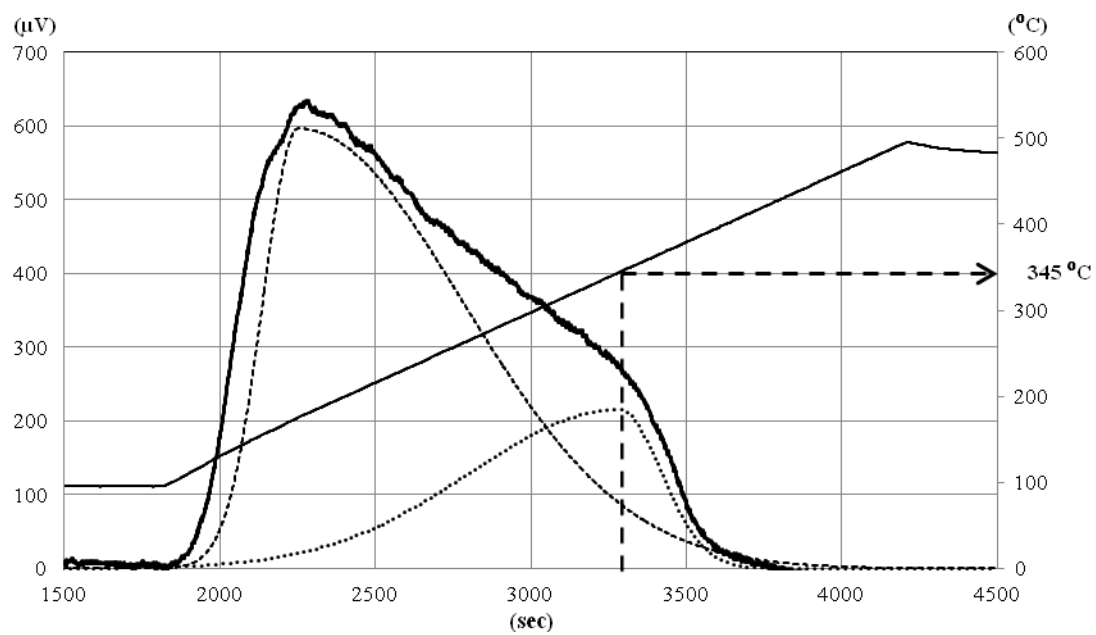

Figure C1 NH$_3$-TPD profile of TiO$_2$ support.

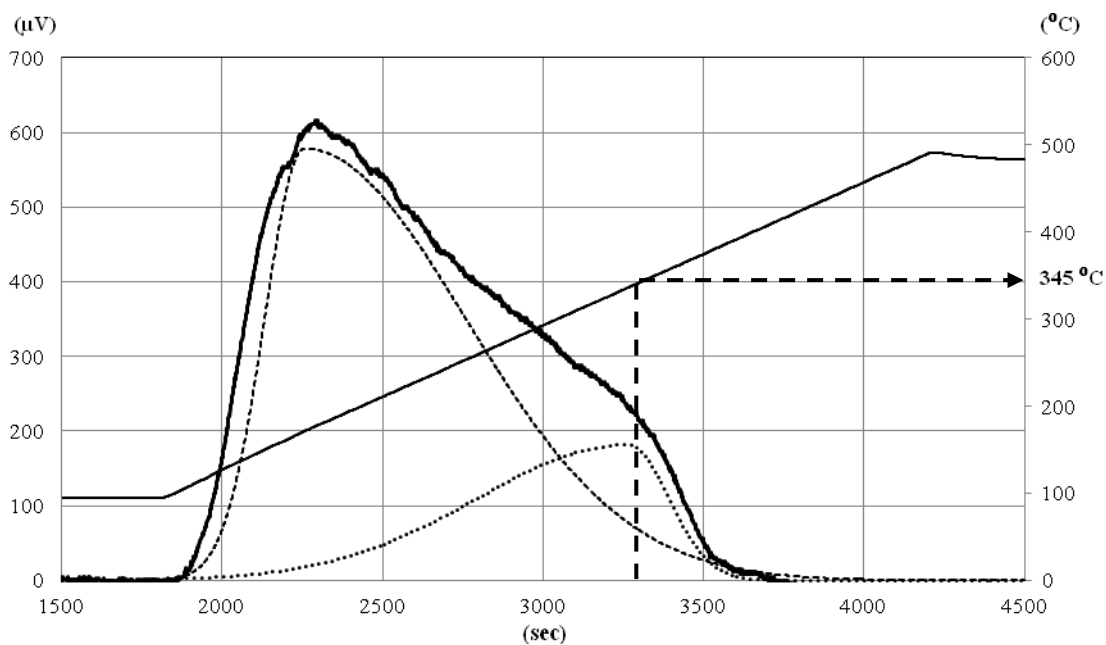**Figure C2** NH$_3$-TPD profile of 3V7W10Mo#1 catalyst.

Figure C3 NH$_3$-TPD profile of 3V7W10Mo#2 catalyst.
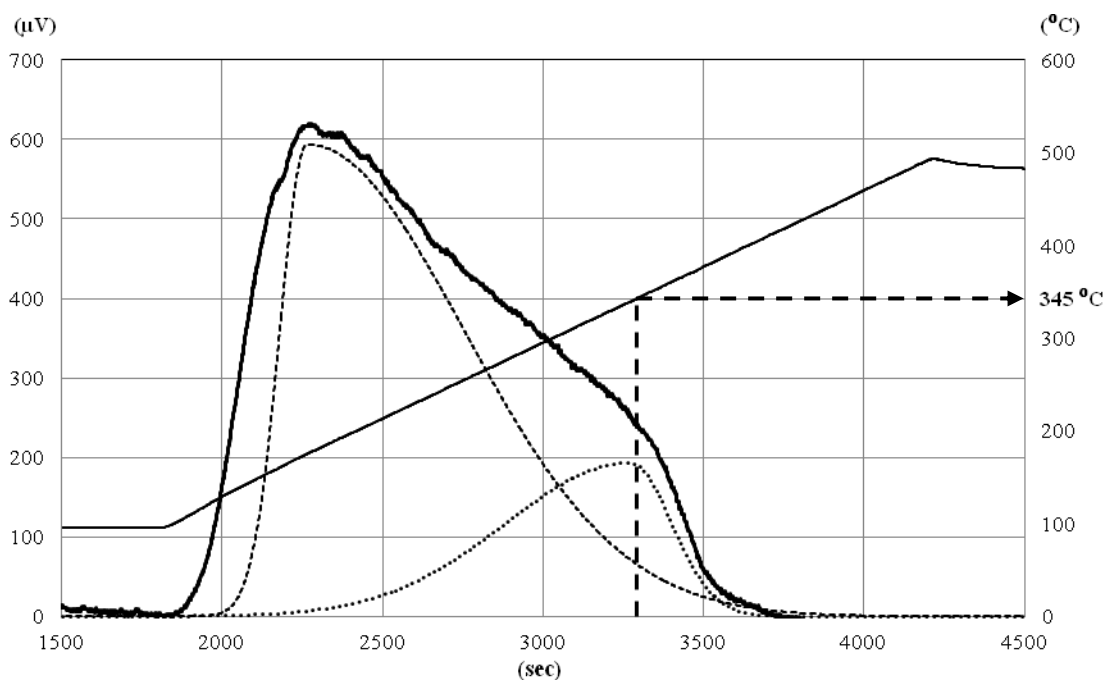
Figure C4 NH$_3$-TPD profile of 3V7W10Mo#3 catalyst.
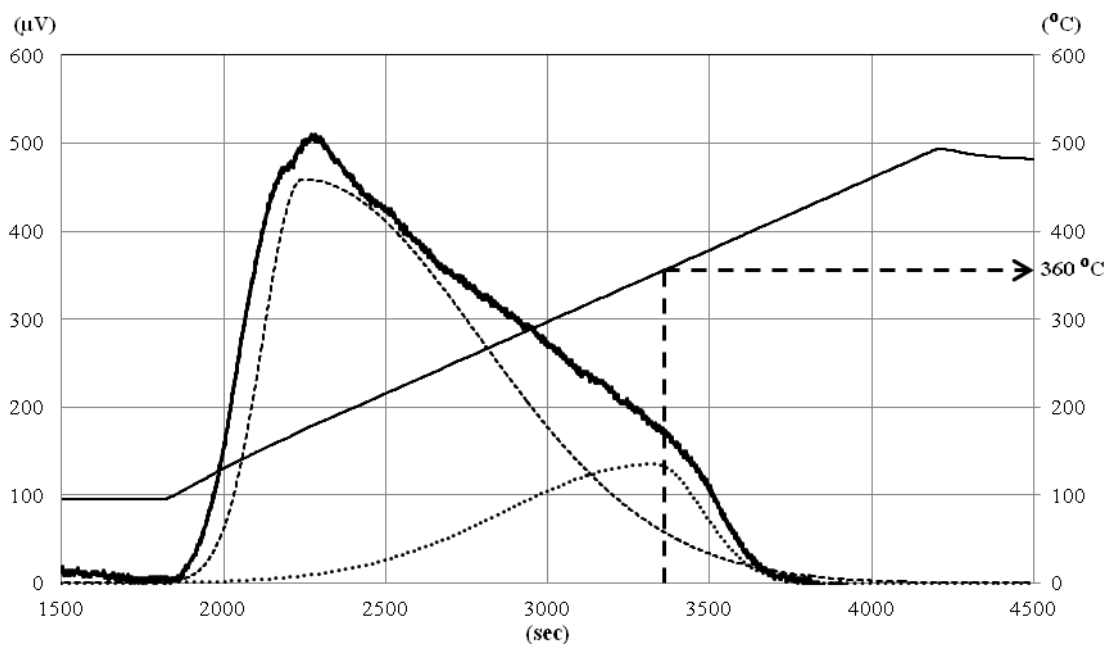

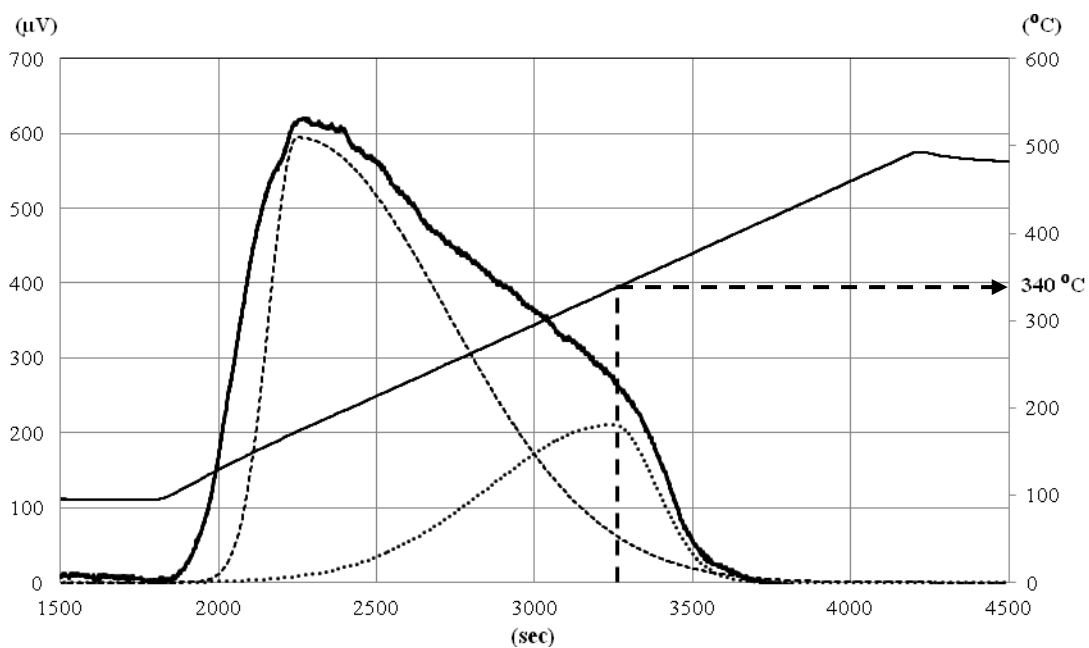**Figure C5** NH$_3$-TPD profile of 3V7W5Mo#2 catalyst.

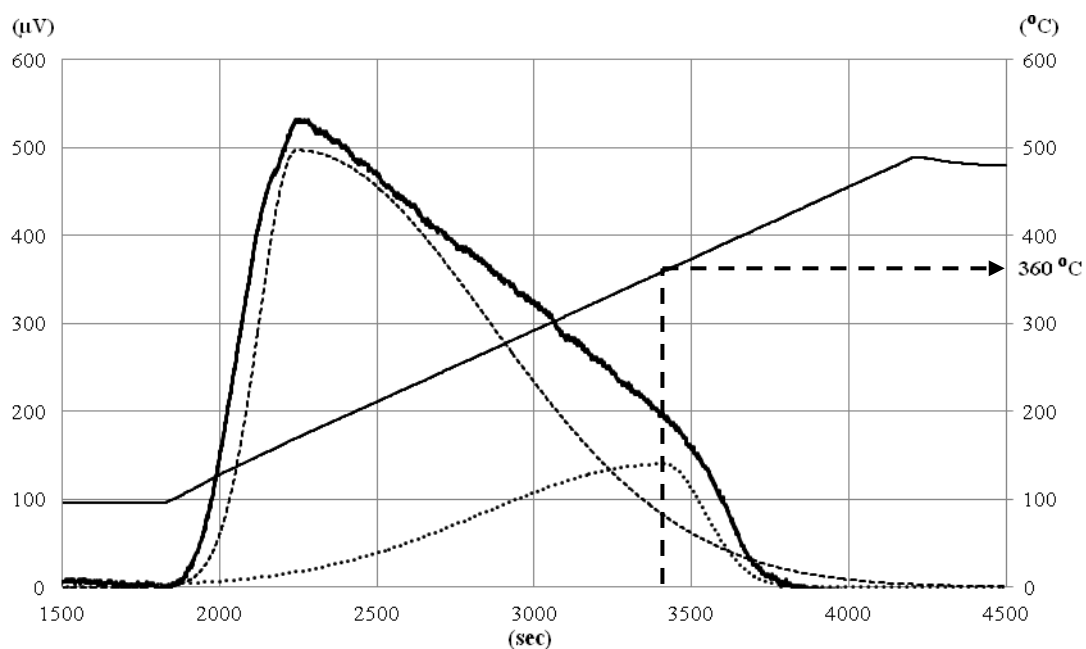**Figure C6** NH$_3$-TPD profile of 3V3.5W10Mo #2 catalyst.

Figure C7 NH$_3$-TPD profile of 3V3.5W5Mo #2 catalyst.

Table C1 Reported total peak of all catalysts.

Catalyst Sample	Amounts of acid site (μmol H^+/g)	Amounts of strong acid site (μmol H^+/g)
TiO_2	377	-
3V7W10Mo#1	378	94
3V7W10Mo#2	385	91
3V7W10Mo#3	380	88
3V7W5Mo#2	388	78
3V3.5W10Mo#2	390	87
3V3.5W5Mo#2	379	78

APPENDIX D

LIST OF PUBLICATION

Kietlada Warinsirirux and Tharathon Mongkhonsi. The selective catalytic reduction of nitrogen oxide by ammonia over V_2O_5-MoO_3/TS-1 catalysts. Thai Institute of Chemical Engineering (TIChE), November, 2011, Ref. NO. cr-006

VITA

Miss Kietlada Warinsirirux was born on May 03, 1988 in Bangkok, Thailand. She finished high school from Potisarn Pittayakorn School, Bangkok, and graduated the bachelor's degree of Chemical Engineering, Mahidol University, in 2010. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2010.