คุณลักษณะและบทบาทของสปีชีส์บนพื้นผิวในปฏิกิริยารีดักชันแบบเลือกเกิดของไนตริกออกไซด์โดยใช้โพรพีนบนตัวเร่งปฏิกิริยาซิลเวอร์บนตัวรองรับ อะลูมินาโดยเทคนิคโปรแกรมอุณหภูมิ

นายนัสธยา เกียรติศิริกุล

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CHARACTERISTICS AND ROLES OF SURFACE SPECIES IN C_3H_6-SCR OF NO OVER A Ag/Al_2O_3 CATALYST BY TEMPERATURE PROGRAMMED TECHNIQUE

Mr. Natthaya Kiattisirikul

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ในงานวิจัยนี้ พฤติกรรมของสารบนพื้นผิวที่เกิดขึ้นบนตัวเร่งปฏิกิริยาซิลเวอร์บนตัวรองรับอะลูมินาในปฏิกิริยารีดักชันแบบเลือกเกิดของไนตริกออกไซด์โดยใช้ไฮโดรคาร์บอนได้ถูกศึกษาผ่านเทคนิคโปรแกรมอุณหภูมิ เมื่อใช้โพรพีนเป็นแบบของสารรีดิวส์ ชุดการทดลองที่มี 3 ขั้นตอนต่อเนื่องกัน ประกอบด้วย ขั้นตอนการเกิดปฏิกิริยา ขั้นตอนทำให้หลุดออกแบบโปรแกรมอุณหภูมิ และขั้นตอนการออกซิเดชันแบบโปรแกรมอุณหภูมิ แสดงให้เห็นว่ามีสารบนพื้นผิวอย่างน้อย 5 สปีชีส์ซึ่งเกิดขึ้นทั้งในขั้นตอนทำให้หลุดออกแบบโปรแกรมอุณหภูมิ และขั้นตอนการออกซิเดชันแบบโปรแกรมอุณหภูมิ จากการทดสอบรีแอคติวิตี้ของสารบนพื้นผิวบนตัวเร่งปฏิกิริยาซิลเวอร์บนตัวรองรับอะลูมินาและซิลเวอร์บนตัวรองรับซิลิกาแสดงให้เห็นว่ามีเพียงสารบนพื้นผิวเพียง 2 ชนิด คือ สารที่สามารถหลุดออกที่อุณหภูมิต่ำและสารที่ต้องถูกออกซิไดซ์ด้วยออกซิเจนที่อุณหภูมิสูง ที่แสดงบทบาทสำคัญในการสร้างไนโตรเจน ดังนั้นกลไกการเกิดปฏิกิริยาประกอบด้วย 2 กลไกหลัก คือ การสลายตัวและการเกิดรีดักชันของไนตริกออกไซด์ นอกจากนั้นผลที่ได้ยังแสดงให้เห็นว่าสารที่ต้องถูกออกซิไดซ์ด้วยออกซิเจนที่อุณหภูมิสูงปรากฏครั้งแรกบนบริเวณเร่งของซิลเวอร์หลังจากนั้นมีการย้ายไปอยู่บนบริเวณเร่งของอะลูมินา และเกิดปฏิกิริยากับแก๊สผสมของไนตริกออกไซด์กับออกซิเจนเพื่อสร้างสารที่สามารถหลุดออกที่อุณหภูมิต่ำ ดังนั้นเทคนิคโปรแกรมอุณหภูมิไม่ได้ใช้เพื่อศึกษาพฤติกรรมของสารบนพื้อนผิวเพียงอย่างเดียวแต่ยังนำมาประยุกต์ในการศึกษาถึงตำแหน่งของสารบนพื้นผิวที่เกิดขึ้น

ภาควิชา……..วิศวกรรมเคมี…….… ลายมือชื่อนิสิต…….
สาขาวิชา……วิศวกรรมเคมี……. ลายมือชื่ออาจารย์ที่ปรึกษา……..
ปีการศึกษา…….2545…….. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม……..

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NATTHAYA KIATTISIRIKUL: CHARACTERISTICS AND ROLES OF SURFACE SPECIES IN C_3H_6-SCR OF NO OVER A Ag/Al_2O_3 CATALYST BY TEMPERATURE PROGRAMMED TECHNIQUE. THESIS ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., THESIS COADVISOR: DR.CHOOWONG CHAISUK, Dr.ENG., 76 pp. ISBN 974-17-4518-4

Abstract

In this thesis, the behavior of surface species which occur in the selective catalytic reduction of nitric oxide by hydrocarbon over Ag/Al_2O_3 catalyst under excess oxygen was investigated through the Temperature Programmed Technique. With propene as a model reductant, and experimental set of three continuous steps containing reaction step, temperature programmed desorption step and temperature programmed oxidation step shows that there are at least five types of surface species occurred on Ag/Al_2O_3 both TPD and TPO step. From the reactivity tests of surface species on Ag/Al_2O_3 and Ag/SiO_2 indicate that only two surface species, S_{TPDL} and S_{TPOH}, play an important role in the production of N_2. Hence, the reaction mechanisms consist of two pathways including the decomposition of S_{TPDL} species and the NO reduction of S_{TPOH} species. Moreover, the results show that the S_{TPOH} species first occurred on silver active site after expose to the reactant gases and then move to the alumina active site. In addition, some of S_{TPOH} species can react with $NO+O_2$ to form the other surface species (S_{TPDL}). Therefore, the Temperature Programmed Techniques do not use only to characterize the behavior of surface species but also apply to investigate the appeared position of surface species.

Department……Chemical Engineering… Student's signature…….
Field of study…Chemical Engineering… Advisor's signature…….
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Finally, he would also like to manifest his greatest gratitude to his parent and his family for their supported and encouragement.

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CHAPTER I

INTRODUCTION

Air pollution is problem of general interest because polluted sources have sharply increased in many years ago. The origins of pollutants that are cause of this problem divided into two kinds of sources dependent on characteristic movement, i.e. mobile source and stationary source [1]. The pollutants and other compounds in exhaust gases consist of principally primary pollutants, unburned hydrocarbon (HCs), carbon monoxide (CO), sulphur oxides (SO_x) and nitrogen oxides (NO_x), in addition to the other compounds such as water, hydrogen, nitrogen and etc.

Emissions of nitrogen oxides that are generated primarily from both stationary and mobile sources are important air pollutants. Their effects are reported to contribute to a variety of environmental problems, including acid rain and acidification of aquatic systems, because it is a strong oxidant and soluble in water and can be oxidized within the atmosphere to form nitric acid (HNO_3). Moreover, it is cause of the harmful impact for the respiratory system of human. The formation of NO_x is occurred in combustion process by combining the N_2 and O_2 present in the air at high temperature [1], as the equation 1.1. However, if a compound in combustion process has bound nitrogen, NO_x is readily formed at much lower temperature through an oxidation process.

$$O_2 + N_2 \rightarrow NO_x \quad (1.1)$$

Nitrogen oxides are formed at two stages during combustion:

1. The reaction of oxygen with nitrogen compounds in the fuel - this is termed fuel NO_x;

2. The reaction of nitrogen with oxygen in the combustion air - this is termed thermal NO_x;

The relative contribution of fuel and thermal NO_x depends on the type of fuel being used and the operating conditions.

It is not possible to reduce the nitrogen content of the fuel by physical cleaning as it is combined within the organic matter of the fuel, and at present there are no commercially available methods to reduce organic nitrogen. Hence, the emissions of NO_x generated during the combustion process can be reduced, as with SO_2, by treating the flue gases. For the above reasons, NO_x emissions are regulated in two ways before the flue gases release to environment.

- Preventing the production and release of nitrogen oxides during combustion, i.e. stages combustion and fluidized bed combustion (FBC)

- Removal of nitrogen oxides after combustion, i.e. selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR) and activated carbon process.

However, the major disadvantages of regulations during combustion are the loss of energy consumption to eliminate NO_x at high temperature, and these processes are used with only stationary source. Therefore, the other method such as catalytic technology has been developing in the present time, because it is applied to control the emissions of NO_x both stationary and mobile sources. The SCR of NO_x using NH_3 was first discovered in 1957 [2]. It was discovered that NH_3 can react selectively with NO_x to produce N_2. Nonetheless, applied NH_3 for management of NO_x has some disadvantage including undesirable product, i.e. NO_2, corrosion and fouling [1]. Until the early 1970, the reduction of the emission of NO_X by using HC became an important control issue. The other catalysts were investigated for use in SCR and the catalysts are divided into three major groups dependent on catalyst performance as shown in Fig.1.1 [3].

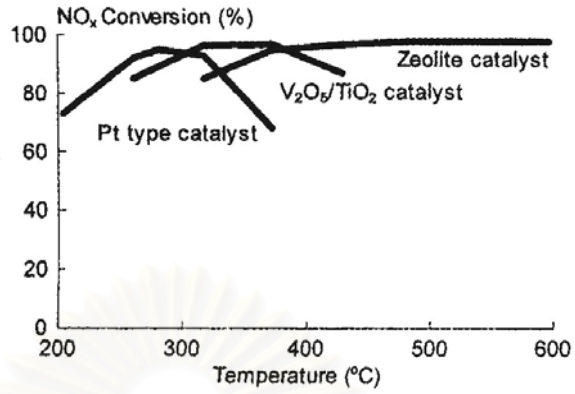

Figure 1.1 Three major families of SCR catalyst [2].

The various characteristics of these catalyst families as described manufacture are given in Table 1.1 [2].

Table 1.1 Operating characteristics of different SCR catalyst.

Medium temperature - VNX^{TM} catalyst (V_2O_5/TiO_2)
- 260-425°C
- most broadly used
- sulfur tolerant
High temperature - ZNX^{TM} catalysts (zeolite)
- 345-590°C
- very high NO conversion
- sulphur tolerant above 425°C
Low temperature - LT catalyst (Pt-based)
- 150-300°C
- narrow temperature window
- temperature window shifts
- no sulphur tolerant

Certainly, no suitable catalyst is used to control the emission of NO_x, because each catalyst shows both advantage and disadvantage [4]. Therefore, the procedures of research about SCR are separated to two parts: (1) to study and improve the conventional catalysts and (2) to develop and design the modern catalyst for the SCR of NO_x. From the literature reviews, although the development of catalyst is achieved by using promoter to improve the stability with H_2O and sulphur, but the selectivity and activity of this is decreased [5]. Nonetheless, after testing nine different classes of promising catalysts was reported, the other concluded that despite the fact that some NM-containing catalysts, there is no single phase catalyst capable of satisfying the practical demands for NO_x removal. Although the unsuccessful management to control NO_x removal was reported, but the developments are continually studied to select the suitable catalysts which show both high activity and stability for NO_x removal.

In recent year, silver (Ag) is a promising catalyst for HC-SCR of NO_x, because the silver-based formulation is an effective catalyst for NO_x removal from exhaust gases under lean-burn conditions. It shows a good activity and selectivity for the SCR of NO by various hydrocarbons. Several organic compounds such as methane [6-8], methanol [5,10], ethane [7-8], hexane [7], butane [7], propene [9-19], methane [AB25,CT45], ethane [Ab 25,CT45], propane [ab25],CT45, ethanol [11,20-23], decane [24], propane [7-8,19,25-28], octane [7,29] were used as the reductant. Moreover, the other advantageous performance is a broad temperature window and a lower selective harmful product. Also, several studies investigated the activity, selectivity and stability of the silver-based material. At the present time, although many authors have reported to advantages of the silver-based catalyst in the HC-SCR of NO under excess oxygen, the reaction mechanism and active intermediate species are rather complicated and have not been fully elucidated. Typically, application of *in situ* Fourier transform infrared spectroscopy has been only used to predict the reaction mechanism and identify the intermediates [30-39]. The possible simultaneous occurrence of at least two reaction pathways results in complication of the analysis and therefore other procedures have to be made in order to obtain more information.

Temperature programmed technique is one of many method that is useful for investigation the surface species [40-42]. It is noted that IR and TP techniques show the different information. The spectral of IR technique exhibit the formation of surface species but not show quantity of each species. On the other hand, temperature programmed techniques give overall information such as quantity, containing species and etc. Examples of the characterization include the observation of nature of surface species using and experimental set of three steps consisting of reaction step, temperature programmed desorption step and temperature programmed oxidation step. Praserthdan et al. [40] and Isarangura na ayuthatya et al. [41] have used the temperature programmed technique to investigate nature of the surface species in the SCR of NO by C_3H_6 over zeolite- and platinum-based catalysts and they confirm that this method can be employed to indicate classification of the surface species. However, only these methods can not show all information of the surface species. The other method was added to fulfill the result of surface species. Srihiranpullop et al. [43] reported applied physical mixture method to investigate the coke formation and found that this method can be used to determine the appeared position of coke. From this report, the physical mixture may be used to investigate the position of surface species that occur on Ag active sites, interface or alumina active sites.

Hence, in this work we have applied temperature programmed techniques to study nature and reactivity of the surface species on Ag/Al_2O_3 in the SCR of NO by C_3H_6 under lean-burn condition.

Following the above motivation, scopes of this study have to be taken into account.

1. Prepare and characterize Ag/Al_2O_3 in order to use for investigation of the surface species.

2. Study the catalytic behavior in the selective catalytic reduction of NO by propene under excess oxygen over Ag/Al_2O_3 catalyst towards temperature programmed

reaction in order to determine a range of the operating temperature for production of the surface species.

3. Investigate the surface species produced on a Ag/Al_2O_3 catalyst in the selective catalytic reduction of NO with propene under excess oxygen by emphasizing on the temperature programmed techniques as follows:

- Study the nature of surface species by an experimental set consisting of three continuous steps including reaction step, temperature programmed desorption step and temperature programmed oxidation step.

- Study the reactivity of surface species to various oxidizing gases by application of temperature programmed oxidation technique

- Study the characteristic of surface species using the physical mixture.

The present research work is divided into five chapters. To accommodate a variety of background of readers, it begins with introduction that is necessary for the understanding of emission control of NO_x in chapter I. Chapter II is concerned with literature reviews of HC-SCR of NO_x over Ag-based catalyst under lean burn condition. An experimental system including catalyst preparation, catalyst characterization and catalyst activities and characterization of surface species is reported in chapter III. Chapter IV demonstrates the experimental results and discussion. Finally, the conclusions and recommendations are shown in chapter V.

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CHAPTER II

SELECTIVE REDUCTION OF NO_x WITH HYDROCARBON OVER Ag-BASED CATALYST UNDER LEAN-BURN CONDITION

The SCR of nitrogen oxides by hydrocarbons has attracted much attention recently because it has the potential ability to remove nitrogen oxides from diesel exhaust and oxygen rich flue gases. Held et al. [44] and Iwamoto [45] first reported some success using zeolite-based catalyst for lean de-NO_x. However, the hydrothermal resistance of these materials is usually unsatisfactory. After that, the other active catalysts such as platinum group materials (PGMs) [46], based oxide/metals have been investigated as de-NO_x catalyst to improve the stability problem. PGMs are inefficient at moderate and high temperatures, pioneering work by Hamada et al. [47] and Obuchi et al. [46] described that these metals could catalyze NO_x reduction by hydrocarbon at low temperature (typically below 300°C). Although these catalysts exhibited significant activities for the same reaction, but the problem of selectivity was observed. At low temperature, a significant amount of NO is converted to N_2O rather than N_2. The others base oxides/metals (e.g. Al_2O_3, TiO_2, ZrO_2, MgO and these oxides promoted by, e.g. Co, Ni, Cu, Fe, Sn, Ga, In as well as Ag compounds) are active catalysts for HC-SCR of NO_x [48-52].

Even though some interesting activities were claimed, there is not sufficient evidence for possible application of such systems under real exhaust condition. In fact, even though some increase of thermal/hydrothermal stability could be achieved, the activities generally poorer compared to the Cu-ZSM5 system. Therefore, many works are focus to find the new catalyst or improve the properties of primary catalysts. Within several materials, Ag-based catalysts appear to be the most promising materials because they show high activity and selectivity to produce N_2 [36]. These include: (1) appreciable activity between 300-600°C and wild temperature windows as shown in Figure 2.1; (2) stability with water and (3) a little selectivity towards dinitrogen formation.

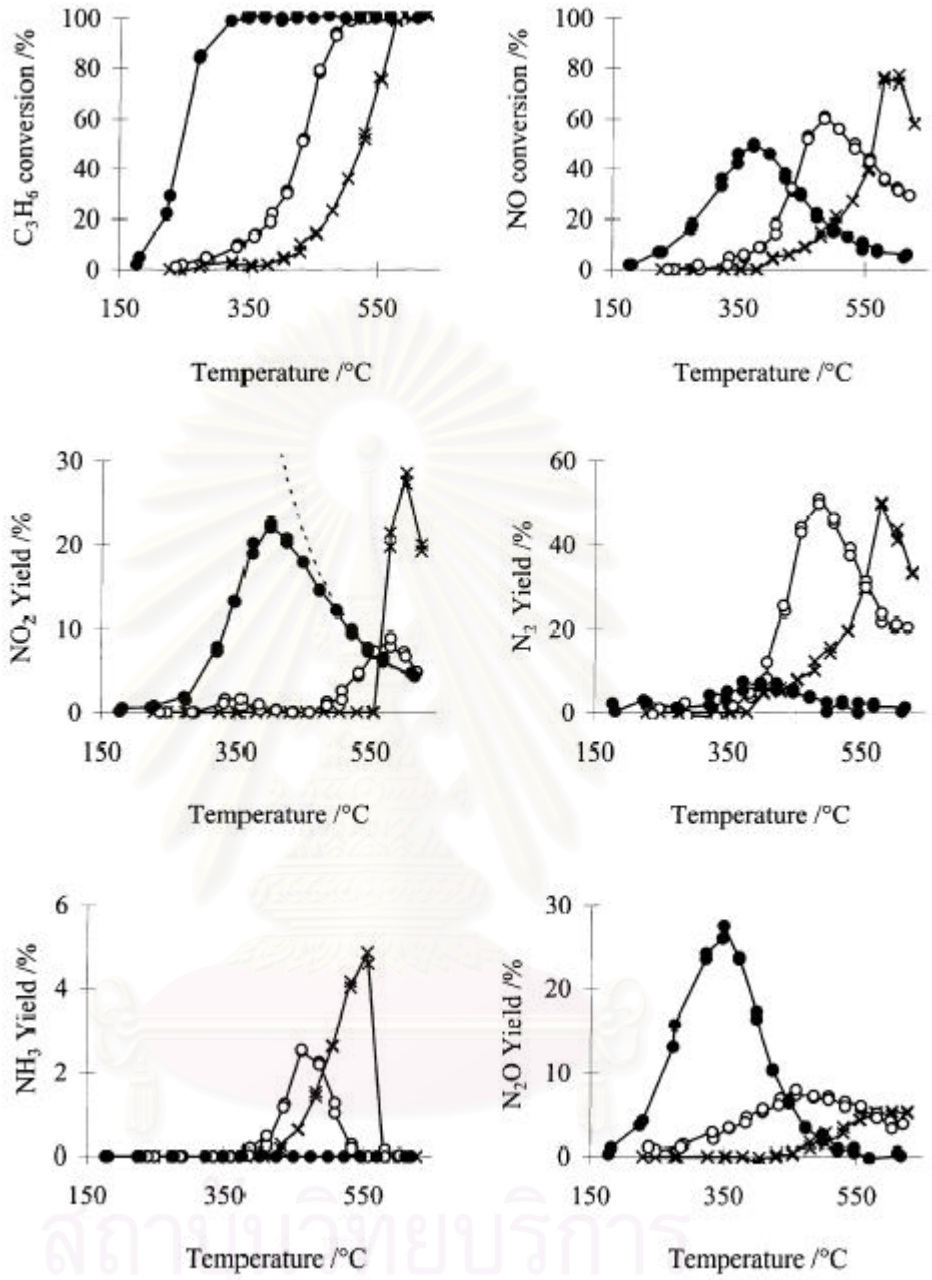


Figure 2.1 C_3H_6-SCR of NO over (×) γ-Al_2O_3, (○) 1.2% Al_2O_3, and (●) 10% Ag/Al_2O_3 catalysts as a function of temperature. Feed: 500 ppm. NO + 500 ppm. C_3H_6 + 2.5% O_2/He, W/F = 0.06g s cm^{-3} (GHSV ~ 50000 h^{-1}). The dotted line in the plot giving the NO_2 yield represents the thermodynamic limit associated with the reaction NO + ½ O_2 ⇔ NO_2 [36].

At the present time, although many authors have reported to advantages of the silver-based catalyst in the HC-SCR of NO under excess oxygen, the reaction mechanism and active intermediate species are rather complicated and have not been fully elucidated. Although the success of HC-SCR still lies somewhere in future, it is now timely to assess the state-of-the-art in terms of our fundamental understanding. In this review, we critically evaluate the published work on the experiment information currently available on Ag-based catalysts including basic concept in the selective catalytic reduction of NO under lean-burn condition over this catalysts and the mechanistic studies of such reaction.

2.1 Overview of SCR over Ag-Based Catalyst

Ag-based catalysts are also among those extensively studies since high activity was reported, particularly when hydrocarbons such as alcohol, alkane, alkene and etc. are employed as reducing agent. The continuous developments of this catalyst have been performed to improve the stability and activity problems.

Originally, the various promoters including Ag were studied to increase the stability and activity of primary catalysts (zeolite based catalyst)). From the literature, clearly the temperatures of highest activity are greatly different dependent on the cations while the maximum activities differed slightly. The order of active temperature regions was Cu < Co < H < Ag < Zn. It was also noted that the wild temperature window over Ag was observed. Moreover, the other metals such as Pd-, Cu- and Au- catalysts are also compared with Ag-based catalyst [49]. In addition, some literature reported regarding unsuccessful improvement of SCR by using single phase catalyst [51]. A variety of catalysts including, which can be classified into: zeolites exchanged with metals ions or just a proton types, alumina and its combination with supported metals or metal oxides, metal oxides other than alumina, metal silicates, and ion exchanged materials other than zeolites. Except for emphasizing differences in the activity among catalysts, general behaviors of the catalysts, such as the active temperature range and the selectivity to N_2O, were similar to that investigates under model gas mixture condition. These results led us to the conclusion that the use of any single phase catalyst, including uniformly mixed

catalysts composed of two different types of catalyst, does not satisfy the practical demand.

While the improvement of activity is executed, the other study about the stability is made [52-55]. Many works attempted to test the stability, because of the typical exhausts to be treated by lean-NO_x catalysts contain up to 10 vol. % of water and up a few hundred parts per million of SO_2. The effect of water on HC-SCR over Ag and other metal promoted on alumina catalyst was investigated. Alumina-supported silver catalyst exhibited extremely high activities in reducing nitric oxide by organic compound in the presence of water [54]. Normally, high concentrations of water in the feed induce a significant deactivation of most catalysts when using light alkenes or alkanes as reductants; however, a high activity can be maintained when oxygenated molecules are used. The inhibition by water is most likely to be due to competitive adsorption between water and one or more of the reactants. The high polarity of oxygenates probably explains their greater ability to compete with water for adsorption when compared to hydrocarbons. Nonetheless, silver has been chosen to study the effect of cocation in order to limit the migration and the subsequent agglomeration of zeolite based catalyst [53]. The presence of silver is possible to partly prevent the catalyst deactivation and in particular to decrease the inhibiting water effect.

In case of sulphur-tolerance, SO_2 is typically found in lean exhaust streams as a result tolerance of several catalysts. Many published research works reported regarding the SCR of NO_x in the presence of SO_x. An inhibition of the SCR of NO by sulphur dioxide is observed in essentially cases, but its extent dramatically depends on the nature of the reductants and the sulphur concentration. SO_2 is known to react with O_2 and the catalyst surface to form stable sulphate phases under reaction conditions. The formation of these sulphate species brings about a reduction in the number of 'strong' chemisorption sites for NO_x. For Ag-based catalyst, the literature reported both advantage and disadvantage of SO_2. Mostly, the loss of activity for SCR over these catalysts was observed as shown in Figure 2.2 when the SO_2 was introduced in to a system. From the DRIFT studies, the spectra of deactivated silver-alumina material showed the formation of two different types of surface sulphate species. One of surface species was a surface aluminium sulphate whereas the other corresponded

to a sulphate associated with the silver phases [55]. However, the sulphate species was removed by using the thermal decomposition process. On the other hand, some work [19] found that the N_2 yield in the absence of SO_2 is reached almost instantaneously a constant level, which is considerly lower than in the presence of SO_2. A promotion effect on the catalytic activity was shown in Figure 2.3.

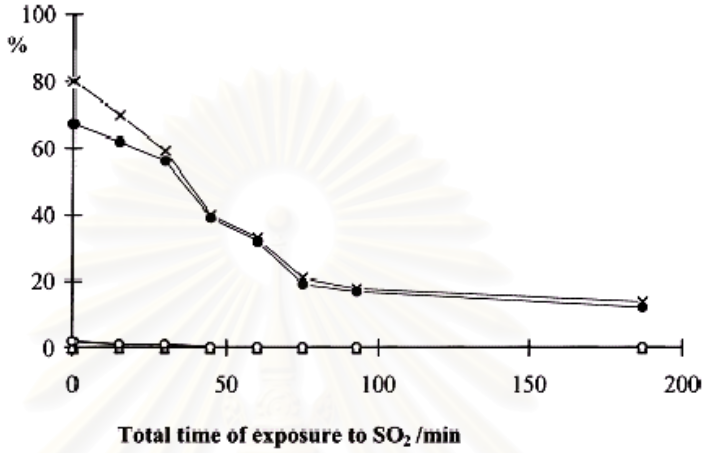


Figure 2.2 N_2 yield (●), N_2O yield (○), NO_2 yield (△) and propene conversion (×) during the propene-SCR of NO over Ag /Al_2O_3 as a function of the time of exposure to 100 ppm of SO_2. T = 486°C, GHSV= 10^5 h^{-1}, 0.1% NO+ 0.1% C_3H_6 +5% O_2 in helium, total flow= 100 ml min^{-1}, 50 mg of catalyst [55].

Focusing on the activity of Ag-based catalyst, the effectiveness of this catalyst for the SCR reaction depends markedly on the nature of reducing agent, its concentration and etc. The effect of the loading of silver on alumina based catalysts for the C_3H_6-SCR of NO has been studied by using loading of silver ranging from 0.5-4wt%. The NO and propene conversions and yields of N_2 and N_2O of these sample at the temperature at which the maximum of NO conversion was obtained in each case are show in Figure 2.4. The T_{max} steadily decreased with increasing silver loading. The highest N_2 yield was obtained with 1% loading. The samples with a loading lower than 2% showed selectivities to N_2 whereas that a higher silver loading also gave significant proportions of N_2O.

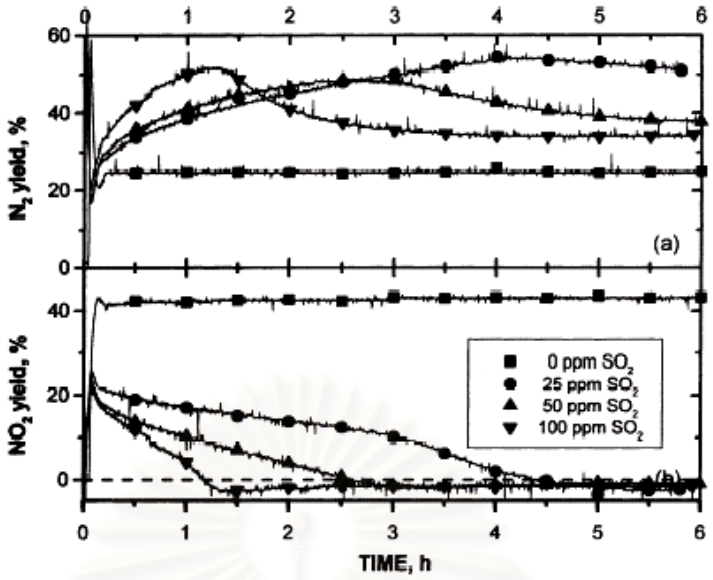


Figure 2.3 N_2 yield % (a) and NO_2 yield % (b) as a function of time-on-stream at various SO_2 feed concentrations between 0 and 100 % ppm (1000 vppm NO, 500 vppm C_3H_6, 500 vppm C_3H_8, 10% (v/v) O_2, balance He, 0.66 g of catalyst, flow rate 500 ml/min). The dashed line in (b) represents the NO_2 produced in the dead volume of the apparatus [19].

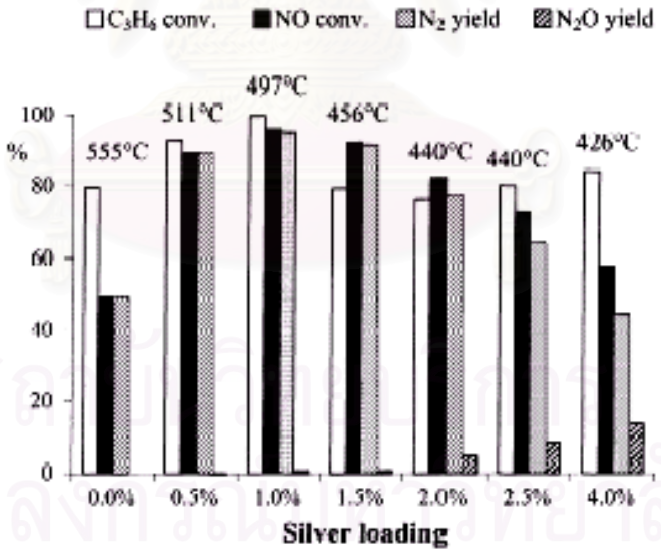


Figure 2.4 Propene-SCR of NO: effect of the loading of silver over Al_2O_3 (Al_2O_3: 115m^2/g). The T_{max} is given at the top of the bars for each silver loading. Feed: 0.1% NO+0.1% C_3H_6+5% O_2 in He; W/F = 0.12 g s cm^{-3}, GHSV = 25,000 h^{-1}[56]

In addition, the above results indicate the promoting effect of silver at intermediate loadings on the SCR reaction. Thus, low Ag samples are active for NO_x reduction, showing NO_x and C_3H_6 conversion profiles at high temperature. On the other hand, the catalytic behavior of the sample with the highest silver loading shows similarities with several studies [56], indicating that low NO_x conversion levels are achieved over alumina-supported samples with relatively high silver loadings, while a relatively higher rate for the non-selective C_3H_6 combustion occurs.

The effect of the other parameter such as space velocity is shown in Figure 2.5. The space velocity affect to both NO and C_3H_6 conversion. When the space velocity increase, both NO and C_3H_6 conversion readily decrease. It indicates that the retention time has great effect to NO-SCR.

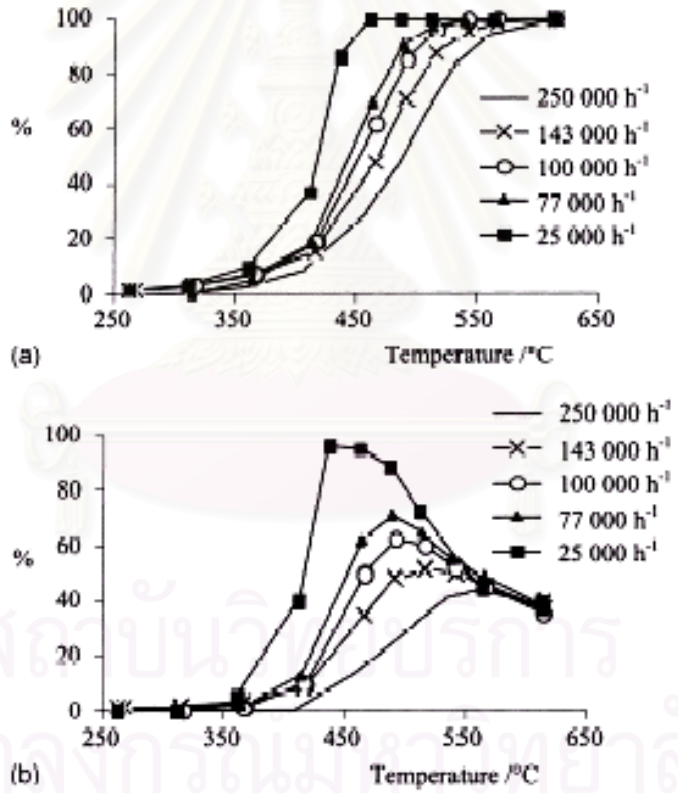


Figure 2.5 (a) Propene conversion and (b) NO conversion to N_2 during the C_3H_6-SCR of NO over 1.2% Ag/Al_2O_3 as a function of temperature and at various GHSV ranging from 25,000 h^{-1} to 250,000 h^{-1}[56]

In case of reducing gases, the different catalytic behavior towards temperature programmed reaction obtained by changing types of reductant, typically results for Ag catalysts tested with a wide range of different organic compounds in some literature are interestingly pronounced. Figure 2.6 shows the conversion of NO in the presence of water vapor when linear alkanes are used as a reductant. Cleary, the carbon number in the hydrocarbon reductant significantly affects NO reduction activity. As the carbon number increased, the temperature range at which NO reduction occurs shifted to the lower temperature region.

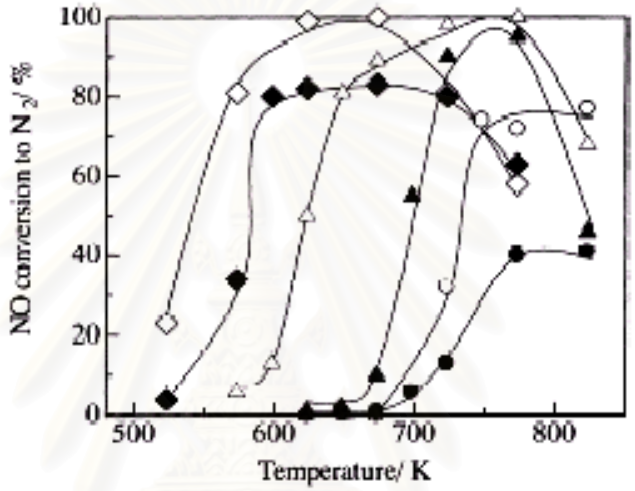


Figure 2.6 NO conversion to N_2 on $Ag–Al_2O_3$ catalyst using various *n*-alkanes: (●) methane, (○) ethane, (△) propane, (▲) *n*-butane, (◆) *n*-hexane, (◇) *n*-octane. Conditions: NO =1000 ppm, *n*-alkane = 6000 ppm, O_2 = 10%, H_2O = 2%, and W/F = 0.12 g s cm^{-3} except for methane-SCR (W/F = 0.9 g s cm^{-3}) [7].

In addition, the effects of kind of organic compounds were tested. The results in which the hydrocarbon (number of carbon = 8) have varied to alkane, alkene, aldehyde, alcohol and acid are shown graphically in Figure 2.8. Octane is much more effective at high temperature while octanol shows high activity at low temperature. The others show moderate NO conversion.

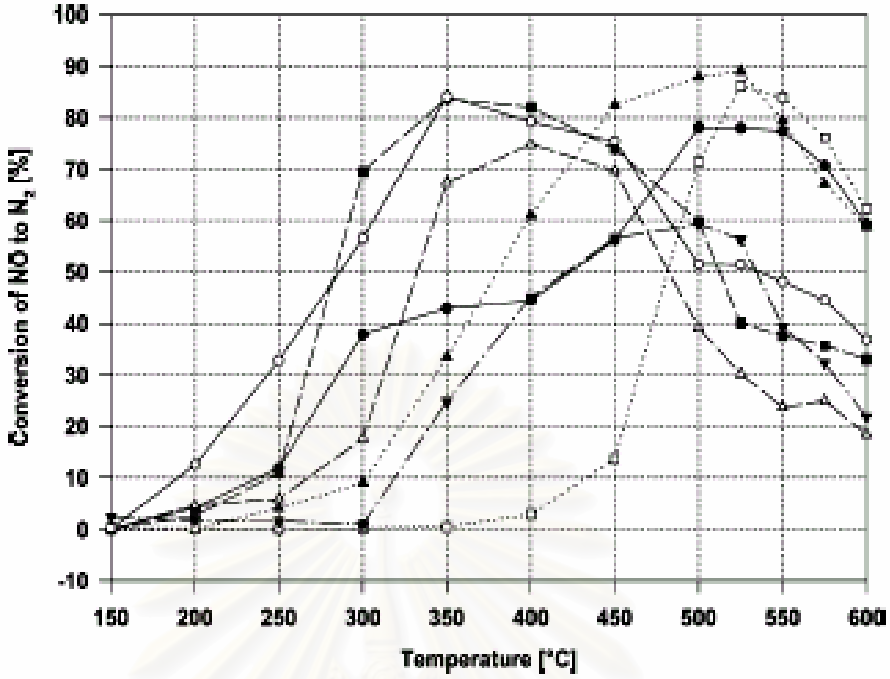


Figure 2.8 NO to N_2 conversions over fresh Ag/Al_2O_3 as a function of temperature using different hydrocarbons as reductants. HC/NO = 6 and GHSV = 60,000 h.1. (□) Propane + propene, (▲) octane, (●) isooctane, (▼) 1-octene, (○) octanal, (■) octanol, and (△) octanoic acid [29].

From described above, this information is some reported regarding the development of SCR over Ag-based catalyst. The obtained available about this basic catalytic behavior encourage in the development of new catalyst formulations sufficiently active and select for the proposed process capable to meet the continuously increased requirement for the clean environment. To improve the catalytic performance, the clarification of the reaction mechanism is essential for future improvement of this catalytic process. Hence, the mechanistic studies of such reaction on Ag-based catalyst are individually in the next section.

2.2 Reaction Mechanistic Studied

There have been a number studies in which the mechanistic aspects of the selective catalytic reduction of NO by hydrocarbon under excess oxygen on a Ag-based catalyst have been considered but yet there is little definitive evidence in support of one model rather than another and as a consequence several mechanisms have been proposed. In general, the reaction mechanism can be subdivided into decomposition mechanism and reduction mechanism. However, the overall reaction mechanism and the rate-determining step of the selective reduction of NO over a given catalyst depend on the nature of the reductant and the experimental conditions. The mechanism is rather complicated and has not been fully elucidated for any given SCR system. Nevertheless, a general picture of the most significant steps likely to occur during the reaction can be drawn from the vast amount of data generated. Alumina and alumina-supported samples have been the focus of most of the studies of reaction mechanisms, generally using propene as reductant.

The role of dioxygen is quite intricate, as it strongly favours the reduction process over most catalytic formulations [58-59]. Most authors acknowledge that the two main functions of O_2 are the oxidation of NO and of the reductant to form various reaction intermediates. Oxygen may also have a role to play in preventing coking of the catalyst surface, especially in the case of strongly adsorbing hydrocarbons such as alkenes.

Since the reaction orders for N_2 formation with respect to both NO and propene are usually close to zero on alumina-based materials [60], the formation of strongly bound reaction intermediates is expected.

Reaction mechanism over oxides: NO reaction pathway

In the absence of O_2, NO only weakly adsorbs on most catalysts surfaces [61-62]. On the contrary, strongly bound nitrite and nitrates are formed in NO/O_2 mixtures. Several literatures reported regarding the reduction of surface species with nitric oxide. Sadykov et al. [63] showed that the decomposition temperatures of strongly bound ad-NO_x species corresponded well to the onset of propane-SCR

activity over numerous catalytic formulations. For alumina and silver/alumina, Shimizu et al. [35,64-65] clearly showed that nitrate species were converted to N_2 during exposure to the reductant at rates that were similar to those of the steady-state reduction of NO. These data strongly support the conclusions reached by many research teams on the role of nitrate species as true reaction intermediates in the SCR process over oxides. The formation of ad-NO_x species on surface sites S is therefore proposed to be the first reaction step of NO as shown in equation 2.1.

$$NO(g) + O_2(g) + S \leftrightarrow \text{ad-}NO_x \qquad (2.1)$$

The formation of NO_2 and its role as a reaction intermediate during the SCR reaction has generated much interest. Although the conversion of NO to NO_2 could conceivably be the first step of the CH_4-SCR on some zeolitic materials (e.g. Co/H-ZSM-5 [66]), most selective oxides are not sufficiently active for this reaction to support the formation of NO_2 as a main reaction intermediate.

$$NO(g) + O_2(g) \leftrightarrow NO_2(g) \qquad (2.2)$$

Meunier et al. [36] clearly showed that selective SCR catalysts, e.g. low loading (< 2 wt.%) Co or Ag supported on alumina, are not significantly active for either the oxidation of NO to NO_2 or the reverse reaction at the temperatures at which these materials are active for the SCR reaction. The reverse is true for high loading catalysts (e.g. 10 wt.%), which show good activity for NO oxidation, but are nonselective for the SCR reaction. The high rate of NO_2 formation observed over high loading samples is clearly related to their high activity for hydrocarbon combustion. Furthermore, the ratio of NO_2/NO observed during the course of the SCR reaction over selective catalysts sometimes exceeds that associated with the thermodynamic equilibrium value of equation 2.2, clearly discarding it as the main route to NO_2 [34,36,67]. High yields of NO_2 can be obtained by the oxidation of organo-nitrito compounds and this rather than the direct oxidation of NO to NO_2 is proposed as the most likely route to gas-phase NO_2 [34,36].

Most of the confusion regarding the role of NO_2 originates from the fact that the SCR of NO_2 is much faster than the reaction with NO over unpromoted oxides

such as Al_2O_3 [68]. NO_2 is more reactive than NO and as a result is more likely to react more quickly with the surface of the catalyst to form ad-NO_x species which have been proposed as key intermediates in the reaction. Metals such as cobalt were proposed to promote the oxidation of NO to NO_2, with the reduction of NO_2 then occurring on the Al_2O_3. However, low rates of NO_2 formation have been observed in the absence of reductant over selective SCR catalysts such as low loading Co/alumina. In addition, in situ IR and thermogravimetric data (Figure 2.8) stressed the inability of isolated cobalt ions to promote the formation of ad-NO_x species on alumina [36]. Instead, the key to the high selectivity and activity of promoted alumina catalyst could be attributed to the reactivity of the ad-NO_x species. Note that these highly reactive nitrate species do not migrate onto the support, in contrast to silver-promoted alumina, which promotes the formation of ad-NO_x species on the support [34].

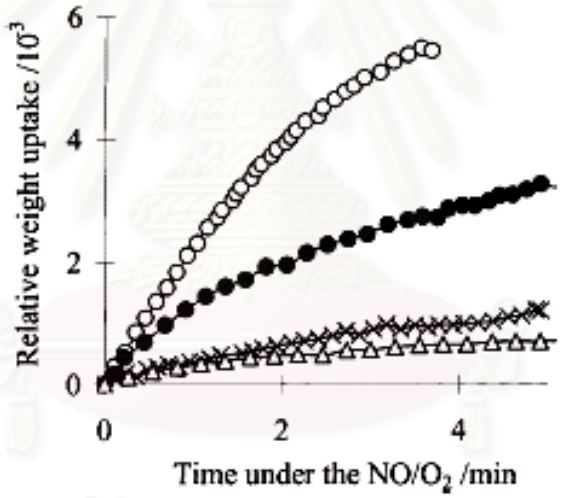


Figure 2.8. Thermogravimetric analysis of the formation of ad-NO_x species at 400 °C over (×) Al_2O_3, (●) 1.2% Ag/Al_2O_3, (○) 10% Ag/Al_2O_3, and (△) 0.4% Co/Al_2O_3 as a function of time. Feed: 0.05% NO + 2.5% O_2 [34].

Reaction mechanism over oxides: hydrocarbon reaction pathway

Similarly to the case of NO, most authors have proposed the formation of strongly bound oxidized species as the first reaction step in the reaction of the hydrocarbon. In addition to the low reaction order for N_2 formation with respect to hydrocarbons [60], this proposition is supported by the fact that oxygenated molecules

react much faster and efficiently than hydrocarbons. For the C_3H_6-SCR of NO over alumina and silver/alumina, Shimizu et al. [35,64,65] clearly showed that acetate surface species were formed by the oxidation of various hydrocarbons and were thereafter consumed at rates similar to that of the reduction of NO. The acetate species or other adsorbed oxidised hydrocarbon species are then believed to react with the surface nitrates (and possibly with gas-phase NO_x) to yield organo-nitrogen species, the exact nature of the organo-nitrogen species remains unclear [69-72]. The formation of the organo-nitrogen species is likely to be the rate-determining step of the reaction. These species are not readily detectable but can be observed during carefully designed transient experiments such as temperature-programmed surface reaction monitored by in situ IR. Organo-nitrogen species can be readily formed non-catalytically by reaction of hydrocarbon, dioxygen and nitric oxide in the liquid or gas phase [70]. In addition, the decomposition products of organo-nitrogen species yield similar products to those observed during the SCR reactions (e.g. cyanide, isocyanates), supporting their role as intermediates. The reactivity of nitromethane has been studied over alumina, over which it is readily decomposed below 200 °C forming isocyanate and ammonia species. NH_3 can be obtained from nitromethane through the tautomerisation to the corresponding oxime followed by dehydration to a nitrile N-oxide (equation 2.3), which isomerise to an isocyanate before yielding a primary amine and NH_3 by hydrolysis (equation 2.4), as suggested over zeolitic materials [72]. Over alumina, the possibility of forming NH_3 from reaction of organo-nitrile N-oxides species was confirmed by Obuchi et al. [73]. The same authors proposed that the organo-nitrile N-oxide were formed from organo-nitroso compounds, via enol and cyanide formation (quation 2.5).

$$–CH_2–NO_2 \rightarrow –CH=NO(OH) \rightarrow –C=N=O \quad (2.3)$$

$$–C=N=O \rightarrow –N=C=O \rightarrow –NH_2 \rightarrow NH_3 \quad (2.4)$$

$$–CH_2–NO \rightarrow –CH=N(OH) \rightarrow –C\equiv N \rightarrow –C=N=O \quad (2.5)$$

The selective reduction of NO with ammonia is an efficient reaction over many catalysts, including alumina and other base oxides and metals. The

intermediacy of NH_3 in the hydrocarbon-SCR reaction has been suggested over zeolites and alumina-based materials [34]. In addition, isocyanate species, readily formed when hydrocarbon reductants were used, were also shown to yield N_2 in the presence of O_2 or NO + O_2 [30-31,74].

Conclusions on the lean-deNO_x reaction mechanism over Ag-based catalyst

The amount of evidence for the intermediacy of strongly bound nitrates and acetates during the SCR of NO with various hydrocarbons or oxygenated reductants is now substantial. However, the other mechanistic steps are still controversial, the reaction between nitrates and acetates appears to be the rate-determining step and, therefore, the surface or gas-phase concentrations of subsequent intermediates are minute.

Nevertheless, the use of transient experiments has shown that reduced species of nitrogen such as –NCO and NH_3 were readily formed, via organo-nitrogen species. Several authors have therefore proposed that the coupling of nitrogen atoms to form N_2 could simply occur via the reaction between the and reduced forms of nitrogen [34]. This observation stresses that the reaction mechanism is very complex since NO will react through a series of parallel and consecutive pathways to form numerous intermediates. Figure 2.10 gives a simplified scheme of a global reaction scheme over oxides/base metal catalysts.

It should be noted that the relevance and rate of each step of the scheme represented in Figure 2.9 depends on the nature of the reductant, the catalyst and experimental conditions. The overall rate-determining step and the surface concentrations of each species may vary accordingly. For instance, Shimizu et al. showed that the chain length of the alkane influences their adsorption reaction properties and therefore the rate at which acetates form [65]. As a result, the proportion of the surface coverage of acetates and nitrate species, which compete for surface sites, varies.

Similar changes in the balance of acetates and nitrates applies in the case of using propene or ethanol over Ag/Al_2O_3, as more acetates and less nitrates are observed in the case of the strongly adsorbing alcohol [75]. This probably explains why isocyanates are more easily observed when using alcohols, as the surface coverage of oxidised ad-NO_x species is lower.

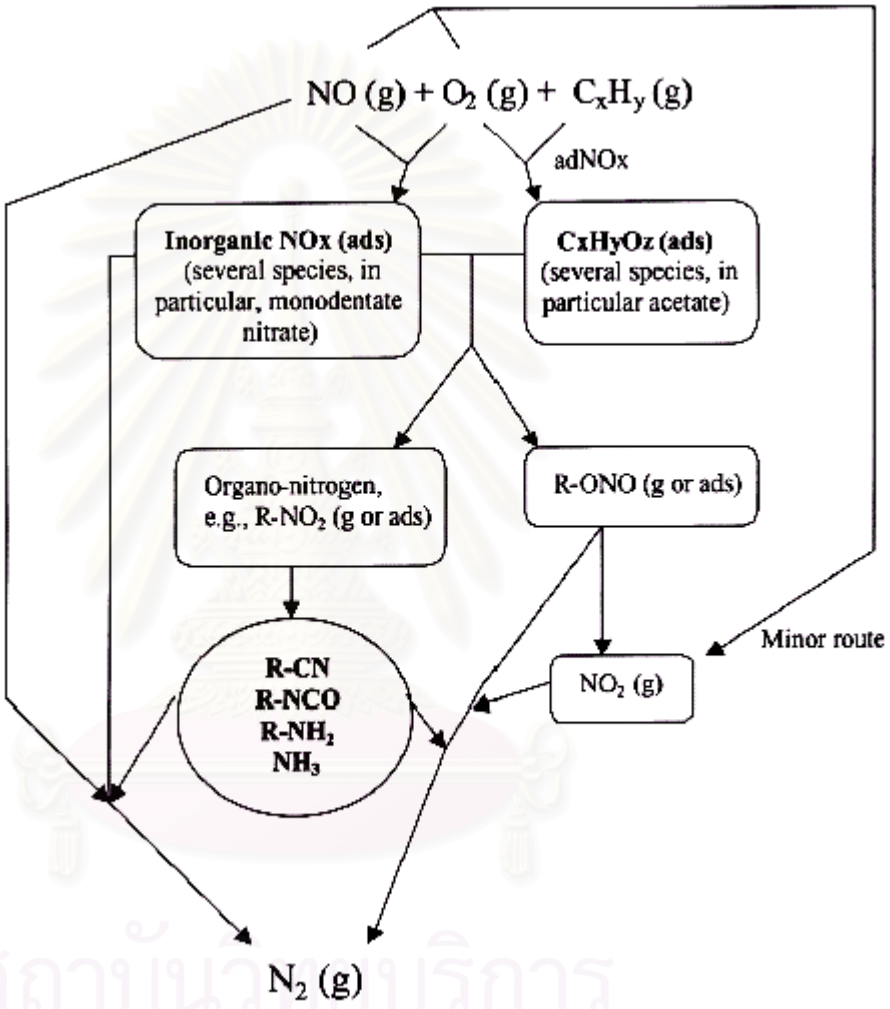


Figure 2.9 Simplified reaction scheme of the C_3H_6-SCR of NO over oxide catalysts giving the nature of the different species likely to be involved. It is proposed that the reduction to N_2 occurs through the reaction of oxidised and reduced (species in shaded circle) nitrogen compounds [34].

In the case of the C_3H_6-SCR of NO over Al_2O_3, the rate of nitrate formation is slower than their rate of consumption, and mostly acetates are observed [34-35]. One of the roles of Ag in Ag/Al_2O_3 catalysts is to promote the oxidation of NO to ad-NO_x species [34], which reside on both the Al_2O_3 and Ag. Yamaguchi [] observed that too

large an increase in the partial pressure of NO over Ag/Al_2O_3 saturated the surface with nitrates, effectively poisoning the sample. Note that such a deactivation was not observed in the case of Co/Al_2O_3 because the Co does not appear to promote the formation of ad-NO_x on Al_2O_3. This may be due to the formation of strongly bound ad-NO_x species on the Co which do not readily migrate to the Al_2O_3 support.

Kameoka et al. [75] also emphasised that nitrates do not all have the same reactivity, and proposed that a monodentate species was the most reactive ad-NOx species over Ag/Al_2O_3. One of the various roles of nitrates is also to facilitate the initial oxidation of the hydrocarbon, as shown by an increase in oxidation rate by ad-NO_x species [35]. Regarding potential intermediates, Zuzaniuk et al. [36] reported that organo-nitro and organo-nitrito needed to be considered differently, since the latter mostly yielded NO_2 as oxidation product, rather than the NH_3 derived from the nitrocompound. Other experimental parameters such as temperature, water vapour pressure will affect the priority of the reactions as reported in Figure 2.9. The possible participation of homogeneous reactions must also be considered, especially at the higher temperatures and bearing in mind that NO and NO_2 are radicular. Yet, it appears the majority of data reported on oxides/base metals are consistent with this scheme. In addition to the possible simultaneous occurrence of parallel reaction pathways over a given type of catalytic sites, it has also to be born in mind that various catalytic phases may be present on a given materials, complicating further the analysis of the system. This is likely to be the case over, e.g. silver/alumina materials with intermediate loadings, as suggested by Meunier et al. [56] as shown in Figure 2.10.

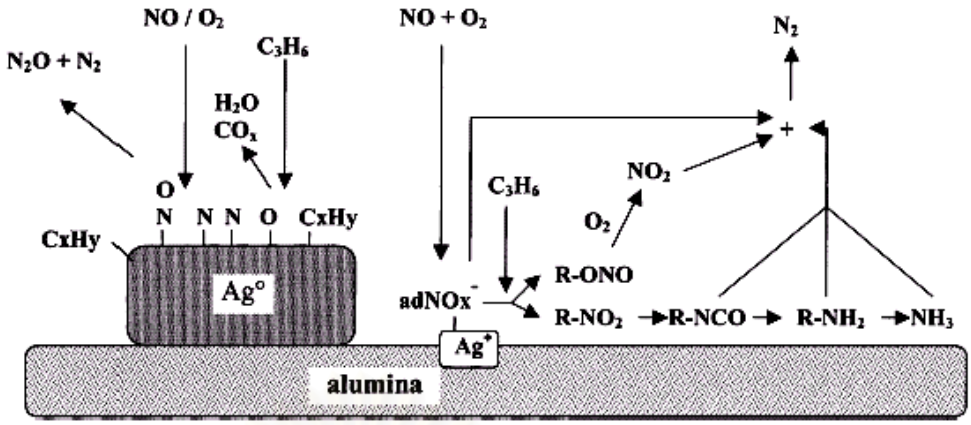


Figure 2.10 The different roles of Ag during the C_3H_6-SCR over Ag/Al_2O_3: large Ag^o particles catalyze the decomposition–reduction of NO, whereas Ag^+ species favors the oxidation of NO to ad-NO_x species, which subsequently react through the intermediacy of organo-nitrogen compounds [34].

CHAPTER III

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work, which is divided into three parts: 1) catalyst preparation, 2) catalyst characterization and 3) catalyst activities and characterization of surface species. The section 3.1 describes the procedure for catalyst preparation. The catalyst characterizations by various techniques including N_2O decomposition method, CO_2 TPD procedure and XRD are explained in section 3.2. Finally, the last section shows the procedures to obtain the catalyst activity and the nature of surface species in SCR of NO by propene.

3.1 Catalyst Preparation

This section is divided into three parts including chemicals, support preparation and preparation of Ag catalyst.

3.1.1 Chemicals

For the preparation of Ag/Al_2O_3 and Ag/SiO_2, analytical grades materials were used in these experiments. Alumina and silica support used in this study are listed in table 3.1.

Table 3.1 Details of chemical reagents used for catalyst preparation

Chemical	Formula	Manufacture
1. Alumina	Al_2O_3	Sumitomo Aluminum Smelting Co., Ltd., Japan (type NKH-3)
2. Silver nitrate	$AgNO_3$	Sigma-Aldrich Chemical Co., U.S.A.
3. Silica	SiO_2	

3.1.2 Preparation of Support

Alumina and silica pellets, spherical shape, were grounded to a required mesh size of 40-60 mesh and then washed by distilled water for 2-3 times to remove the very fine particles and other impurities. Subsequently, they were dried at 110°C overnight and then calcined at 300°C for 2 h in air atmosphere.

3.1.3 Preparation of Silver Catalyst

Ag/Al_2O_3 and Ag/SiO_2 were prepared by the impregnation technique detailed as follows:

1. The amount of silver was calculated just enough for 2 g of the alumina or silica support and then de-ionized water was added until the total volume of the solution became 2 and 1.8 ml for alumina and silica, respectively.

2. 2 g of support was placed in a 50 ml Erlenmeyer flask and then the impregnation solution was gradually dropped into this support using a dropper. Shaking the flask continuously during impregnation was required to ensure the homogenous distribution of metal component on the support.

3. After the incipient wetness impregnation, the mixture of the impregnation solution and the alumina support was left in the atmosphere for 6 h to make a good distribution of metal complex. Subsequently, the impregnated sample was dried at 110 °C overnight in an oven.

4. The dried sample was purged under nitrogen at a flow rate of 60 ml/min with a heating rate of 10°C/min from room temperature to 600°C. When the temperature was reached to 600°C, 100 ml/min of air flow was instead of nitrogen in order to make silver complex become silver oxide, which was in a stable form. The temperature was held at 600°C for 2 h in air atmosphere.

5. After the calcined sample was cooled down, it was stored in a glass bottle into a dessicator for further use.

3.2 Catalyst characterization

This section explains the characterization of Ag-based catalyst including the crystal structure by XRD analysis, the metal active sites by N_2O decomposition and the basicity measurement by CO_2-TPD procedure.

3.2.1 X-ray Diffraction

X-ray diffraction analysis was used to analyze the crystallinity and the structure of a catalyst. The refraction or diffraction of the X-rays was monitored at various angles with respect to the primary beam X-ray diffraction analysis using an X-ray refractometer, SIEMENS XRD D5000, with Ni-filtered CuKα radiation in the 2θ range of 10 to 80°.

3.2.2 Silver Metal Active Sites Measurement by N_2O Decomposition Method

The number of metal active sites were measured by N_2O decomposition technique on the assumption that only one N_2O molecule adsorbed and reacted with two silver metal sites, as the equation 3.1

$$N_2O + 2Ag^{o} \rightarrow N_2 + Ag\text{-}O\text{-}Ag \qquad (3.1)$$

A. Materials

Helium in ultra high purity grade, hydrogen in ultra high purity grade and nitrous oxide in purity grade were used as a carrier gas, a reducing agent and an adsorbent gas, respectively. All gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The extensive diagram of instruments in measurement of the metal active sites is included in Figure 3.1. The amount of the effluent gases was measured by a thermal conductivity detector within a gas chromatograph (GOW-MAC). An operating condition of the gas chromatograph is illustrated in Table 3.2.

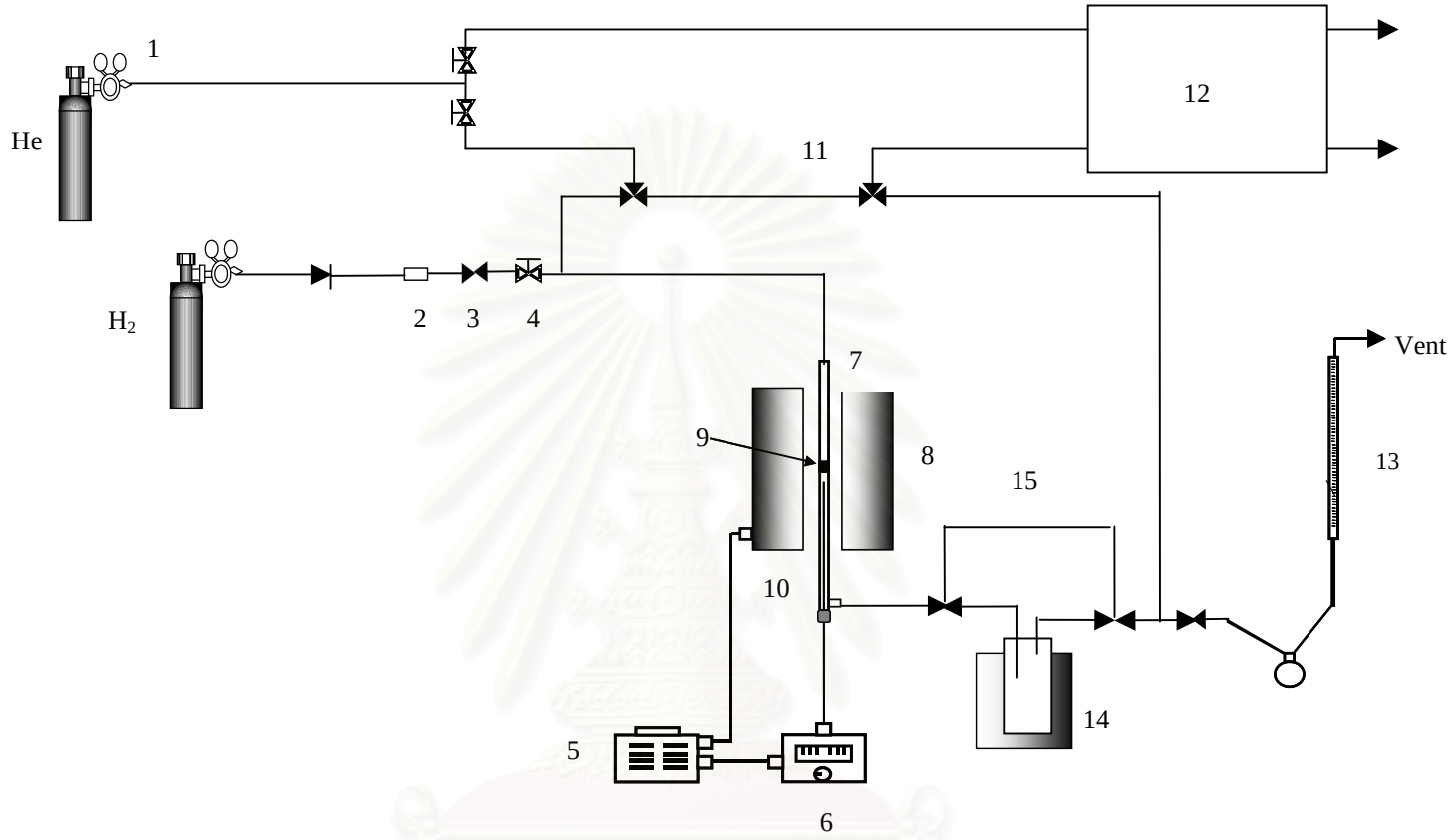
Table 3.2 Operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) for measurement of the metal active sites

Model	GOW-MAC
Detector type	TCD
Helium flow rate	30 ml/min
Detector temperature	30°C
Detector current	80 mA
Packed column	Porapak-QS

C. Procedure

1. 0.1 g of a catalyst sample was placed in a stainless steel tubular reactor. Helium gas was introduced into the reactor at a flow rate of 30 ml/min. The catalyst sample was heated at an increasing rate of 10°C/min until a temperature reached to 300°C, then helium was substituted by hydrogen at a flow rate of 50 ml/min and held at this temperature for 1 h. Subsequently, the catalyst sample was cooled down to room temperature in helium flow.

2. At 150°C at which the catalyst sample was ready to be measured the metal active sites, 50 μl of the purity nitrous oxide gas was injected into the injection port to decompose on the metal surface of the catalyst sample. Injection of nitrous oxide was continuously repeated until the nitrous oxide did not any longer decompose on the



1. Pressure Regulator 2. Gas Filter 3. On-Off Valve 4. Needle Valve 5. Variable Voltage Transformer
6. Temperature Controller 7. Reactor 8. Furnace 9. Catalyst Bed 10. Thermocouple
11. Three-way Valve 12. TCD 13. Bubble Flow Meter 14. Saturator 15. Three-way Valve

Figure 3.1 Flow diagram of measurement of N_2O decomposition and CO_2-TPD

catalyst sample. This situation was occurred when an obtained chromatogram area of any injection, after decomposition of the nitrous oxide pulse in the first injection had proceeded, was kept nearly constant compared with that of the former injection or no nitrogen product was released.

3. The amount of the metal active sites of the catalyst sample will be calculated according to description in Appendix C.

3.2.3 Basicity by CO_2 TPD

A. Materials

Helium in ultra high purity grade and carbon dioxide in purity grade were used as a carrier gas and an adsorbent gas, respectively. All gases used in this experiment were supplied by Thai Industrial Gas Limited.

B. Apparatus

The instruments and the flow diagram of the system to study the CO_2 TPD are shown in Figure 3.1. An operating condition of the gas chromatograph is illustrated in Table 3.3.

Table 3.3 Operating condition of a thermal conductivity detector within a gas chromatograph (GOW-MAC) for measurement of CO_2 TPD

Model	GOW-MAC
Detector type	TCD
Helium flow rate	30 ml/min
Detector temperature	30°C
Detector current	80 mA

C. Procedure

1. 0.1 g of a catalyst sample was packed in a stainless steel tubular reactor. Helium was introduced at a flow rate of 50 ml/min, the catalyst sample was heated up to 500°C at a heating rate of 10°C/min and held for 1 h at this temperature in order to eliminate the adsorbed water. Then, the system was cooled down to room temperature.

2. The sample was purged with 30 ml/min of CO_2 at room temperature for 1 h, and then helium gas was substituted into the reactor at a flow rate of 30 ml/min. After CO_2 adsorption, this sample was heated from room temperature to 500 °C in He atmosphere. The heating rate used in this study is 5°C/min.

3.3 Catalyst Activities and Characterization of Surface Species

For section 3.3, the activity and characteristic of surface species in SCR of NO by propene were studied using temperature programmed techniques.

A. Materials

The gases used in the catalytic activity test are listed in Table 3.4. They were all supplied by Thai Industrial Gas Limited.

Table 3.4 The details of gases used in the catalyst activity test

Gases	Formula	Grade
Helium	He	Ultra high purity
Oxygen	O_2	10% in He
Nitric oxide	NO	1% in He
Propene	C_3H_6	3% in He

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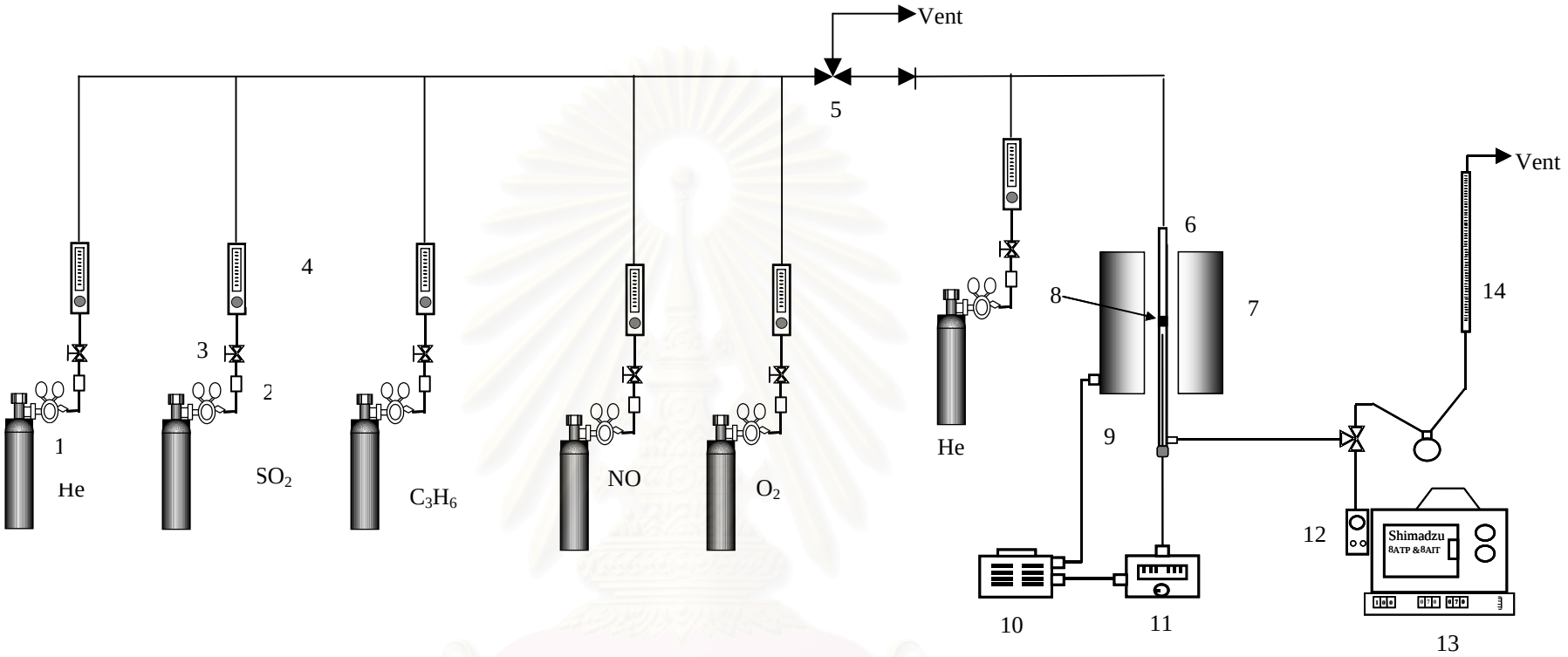

1. Pressure Regulator 2. Gas Filter 3. On-Off Valve 4. Flow meter
5. Three-way Valve 6. Reactor 7. Furnace 8. Catalyst Bed
9. Thermocouple 10. Variable Voltage Transformer 11. Temperature Controller
12. Sampling Valve 13. Gas Chromatography 14. Bubble Flow Meter

Figure 3.2 Schematic diagram of the reaction line for NO and HC conversions analyzed by gas chromatographs equipped with molecular sieve 5A and porapak QS columns

B. Apparatus

A flow diagram of the system for testing the catalytic activity is shown in Figure 3.2. A quartz flow reactor with 0.6 cm inside diameter was used in this experiment. Feed and effluent gases were analyzed by TCD gas chromatographs, SHIMADZU GC8-ATP and SHIMADZU GC-8AIT. An operating condition used in this experiment is given in Table 3.5. This section is divided into two parts including the catalyst activity and the nature of surface species

Table 3.5 Operating conditions of gas chromatographs for the catalytic activity test

Gas Chromatograph	SHIMADZU GC8A-ATP	SHIMADZU GC8A-AIT
Detector	TCD	TCD
Packed column	Molecular sieve 5A	Porapak QS
Carrier gas	He (UHP)	He (UHP)
Flow rate of carrier gas	45 ml/min	85 ml/min
Injector temperature	100°C	110°C
Column temperature	60°C	80°C
Detector temperature	100°C	110°C
Current	80 mA	90 mA
Analyzed gas	O_2, N_2, CH_4, CO	CH_4, CO_2, N_2O, C_3H_6, SO_2

C. Procedure

An experiment for studying catalyst activity behavior

1. 0.4 g of a catalyst sample was packed in quartz tubular down flow reactor. The reactor was placed in the furnace.

2. A gas mixture containing 1000 ppm NO, 1000 ppm C_3H_6 and 5% O_2 diluted in helium at a total flow rate of 200 ml/min (GHSV of 16000 h^{-1}) was used as a model exhaust gas to test the catalytic activity through temperature programmed

reaction. The reaction gases were introduced to the reactor whose temperature was raised from 50 to 700^{o}C stepwise. At each step, the catalyst bed was held at constant temperature until steady state was reached. This was achieved within 20 min. The effluent gases were analyzed by TCD gas chromatographs as shown in table 3.5.

3. These chromatograms were compared with calibration curve to calculate the composition of gases in feeds and effluent gases.

An experimental set for studying the nature of surface species

1. 0.4 g of a catalyst sample was packed in quartz tubular down flow reactor and the height of the catalyst bed was about 0.6 cm. The reactor was placed in the furnace and helium was introduced into the reactor in order to remove the remaining air out of the system.

3. The nature of surface species on the catalyst exposed to the reactants was investigated by an experiment consisting of three steps as follows:

a. Reaction step: A selected reactant gas mixture containing 1000 ppm NO, 1000 ppm C_3H_6 and 5% O_2 diluted in helium at a total flow rate of 200 ml/min (GHSV of 16000 h^{-1}) was used as a model exhaust gas to produce the surface species. This reactant gas mixture was introduced at a given temperature for 2 h. Samples of effluent gases were taken to measure a composition and analyzed by gas chromatograph every 10 min to check the steady state conversions of C_3H_6 and NO at a dosing temperature. When a time on stream was equal to 2 h, the catalyst sample was immediately flushed with helium at the same temperature for 10 min and then cooled down to room temperature.

b. Temperature programmed desorption (TPD) step: After dosing the catalyst in the first step, it was continuously followed by temperature programmed desorption to remove as much of the adsorbed surface species as possible in the same apparatus. During TPD step, temperature was ramped at a constant 5°C/min from 100

to 800°C under 50 ml/min helium flow. The effluent gases were analyzed using two TCD GCs, one equipped with a molecular sieve 5A column for separating O_2, N_2 and CO and a Porapak QS column for separating CO_2, N_2O and hydrocarbons. Peak areas were automatically determined using Shimadzu C-R6A integrator data system. The amount of surface species was calculated from tracers of releasing gases through calibration curves as described in Appendix C. Finally, the catalyst sample was cooled down to room temperature.

c. Temperature programmed oxidation (TPO) step: On completion of the TPD step, a TPO run using oxidizing gases such as 1% O_2 in He was carried out to determine if there were any residual carbonaceous materials on the catalyst. During TPO step, temperature was ramped at a constant 5°C/min from 100 to 800°C under 50 ml/min helium flow. The effluent gases were analyzed using two TCD GCs being the same as the TPD step.

4. It was remarked that an experiment to test a reactivity of the surface species was achieved by using temperature programmed oxidation with changing an oxidizing gases such as $NO+O_2$.

CHAPTER IV

RESULTS AND DISCUSSION

In this research, the characteristic of surface species on the SCR of NO with propene in the presence of excess oxygen over Ag/Al_2O_3 were investigated through temperature programmed techniques. The results and discussion in this chapter were separated into two main parts. In the first section, a basic characterization of a monometallic Ag/Al_2O_3 catalyst is pronounced. Next, the catalyst activity and characterization of surface species are shown in section 4.2. To discuss the behavior of surface species, the reactivity and physical mixture method were used to study the nature of surface species.

4.1 The Characterization of Ag/Al_2O_3 Catalyst

Ag/Al_2O_3 catalyst was first characterized to overview their properties and characteristics. XRD was used to measure the structure of Ag/Al_2O_3 while the desorption of CO_2 was investigated through CO_2-TPD.

4.1.1 X-ray Diffraction Analysis

The crystallinity and structure of pure 2% and 10% Ag/Al_2O_3 catalysts were analyzed by X-ray diffraction (XRD). The same XRD patterns of both are illustrated in Figure 4.1. These spectra are similar with XRD pattern of Al_2O_3 [57] and reveal neither the presence of silver oxide nor metallic silver. This means that the silver particle size may be quite small. Bethke et al. [57] found that XRD of Ag/Al_2O_3 catalysts exhibited the signal, which indicated the absence of Ag^{2+} and small paramagenetic Ag^0 particles. Moreover, they use UV-Vis diffuse to determine the existent silver and they found that Ag/Al_2O_3 catalyst contain small Ag_2O particle isolated Ag^+ atoms.

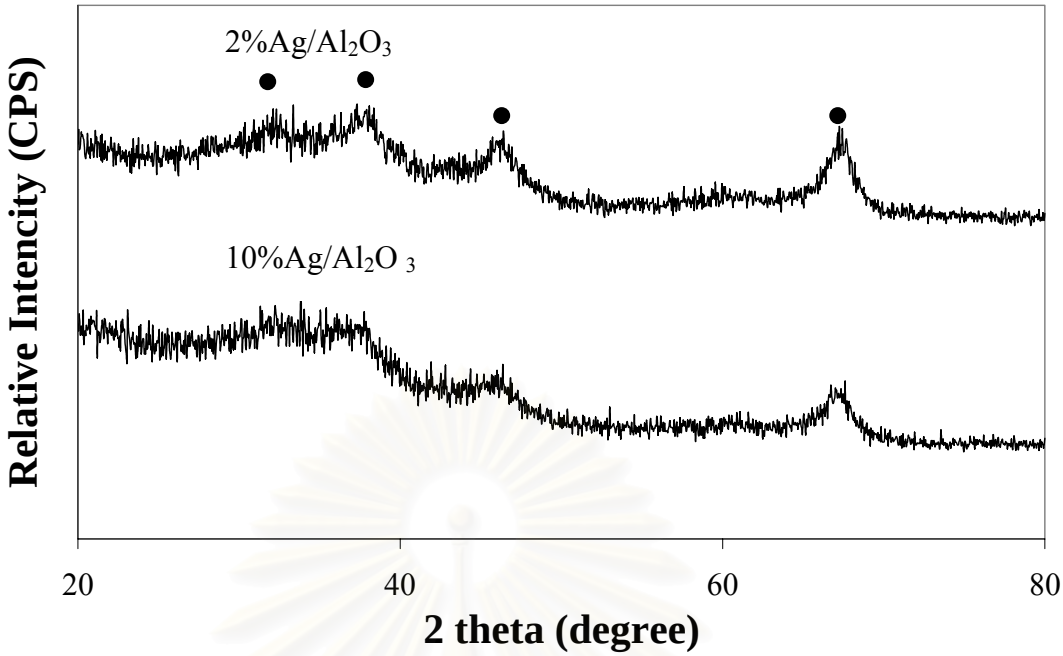

Figure 4.1 X-ray diffraction pattern of 2% and 10%Ag/Al_2O_3 catalysts: (•) γ-Al_2O_3.

4.1.2 The Basicity by CO_2-TPD

In this experiment, the desorption of CO_2 molecule was investigated by using CO_2-TPD technique and this data do not show only basicity behavior but also give information regarding the temperature range for desorption of CO_2 molecule. Figure 4.2 exhibits CO_2-TPD profile of Ag/Al_2O_3 catalyst. This spectrum shows a peak with a maximum at 125°C and a shoulder at 100°C as well as a long tail, extending to 300 °C. It can be implied that a majority of basic sites on our Ag/Al_2O_3 catalyst behaves the weak basic sites.

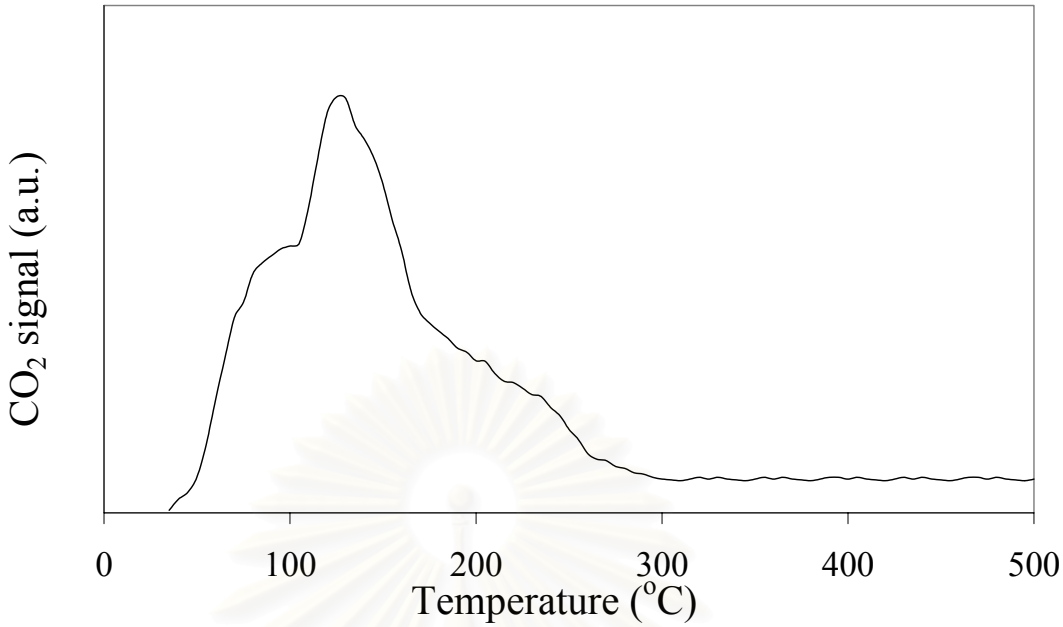

Figure 4.2 Carbon dioxide TPD spectrum of Ag/Al_2O_3 catalyst

4.2 Evaluation of surface species

Before the behavior study of surface species, temperature programmed reaction (TPR) of propene and nitric oxide was made because these data were used to select the temperatures for production the surface species during the reaction steps in the next section. These results do not only show activity behavior but also give information regarding the temperature range. In this part, two concentrations of Ag/Al_2O_3 catalysts were tested the catalytic activity measurement toward TPR.

TPR profiles involving C_3H_6 and NO conversions versus the elevated temperature are shown in Figure 4.3 for the 2 wt% Ag/Al_2O_3 and in Figure 4.4 for the 10 wt% Ag/Al_2O_3. The 2 wt% Ag/Al_2O_3 is an effective catalyst but is active at a high temperature while the difference activity is observed over the 10 wt% Ag/Al_2O_3. This catalyst is active at a low temperature. The overall NO reduction conversion reaches a sharp maximum of approximately 90% at 450 °C and 50% at 350 °C for the 2 and 10 wt% catalysts, respectively. The main products are CO_2 and N_2. No CO is both observed while N_2O product occurs on only high-loading silver material while the other products such as NH_3 and NO_2 could not detect in this experimental. Meunier et al. [36] reported that the formation of various products (NO_2, N_2, N_2O and NH_3) was

observed. The peak for reduction to N_2 occurs about 100 ºC similar to the peak for total NO conversion so that there is some variation of selectivity to N_2O with changing temperature. It is approximately in the range of 15-50%. Both catalysts show coincidence of the onset of NO reduction and C_3H_6 oxidation.

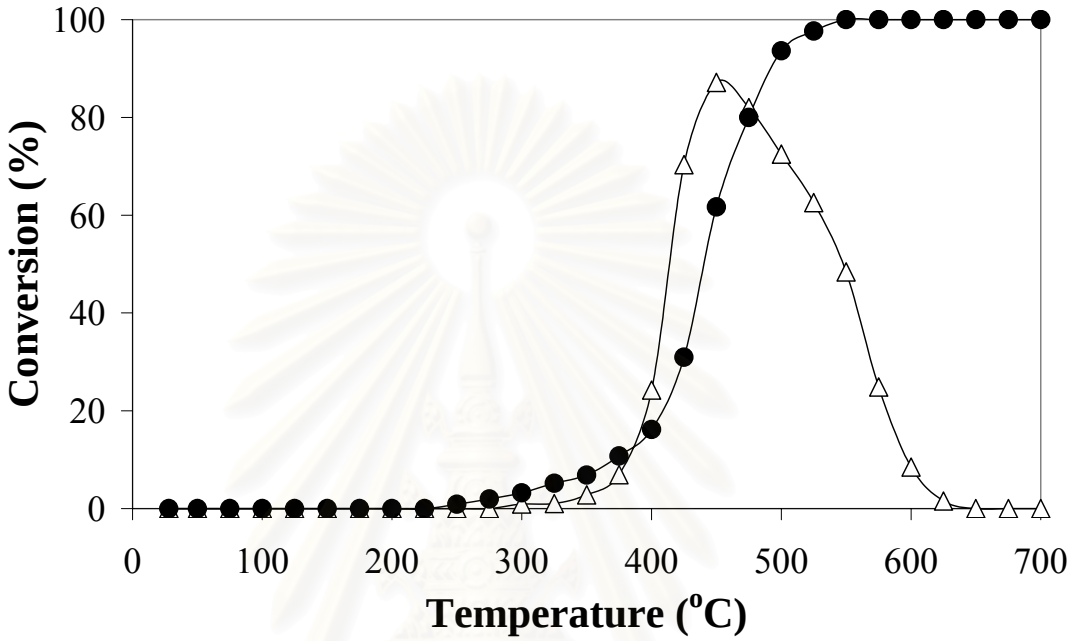

Figure 4.3 The temperature programmed reaction profiles of 2 wt% Ag/Al_2O_3 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion and (△) total NO conversion.

Nevertheless, there is also some difference in the behavior patterns of both TPR profiles. Maximum NO_x conversion is coincident with 100% C_3H_6 conversion for the 10 wt% Ag/Al_2O_3 but not for the 2 wt% Ag/Al_2O_3. The low-loading silver shows occurrence of the maxima for total NO conversion at approximately 100 °C before combustion approaches to completion. These different activity patterns are related to the different of reaction mechanisms, which arise on different catalytic phase. Meunier et al. [36] found that the low-loading silver material exhibited high conversions to N_2 whereas the high-loading sample predominantly yielded N_2O. They proposed that low-loading silver revealed the presence Ag^+ species while high-loading silver showed the presence of oxidic species of silver (as isolate Ag^+ and silver aluminates). This phenomenon is in agreement with the results reported several

authors [36, 77]. Finally, it is significantly noted that 2% Ag/Al_2O_3 gives much more activity and selectivity than 10 % Ag/Al_2O_3 catalysts.

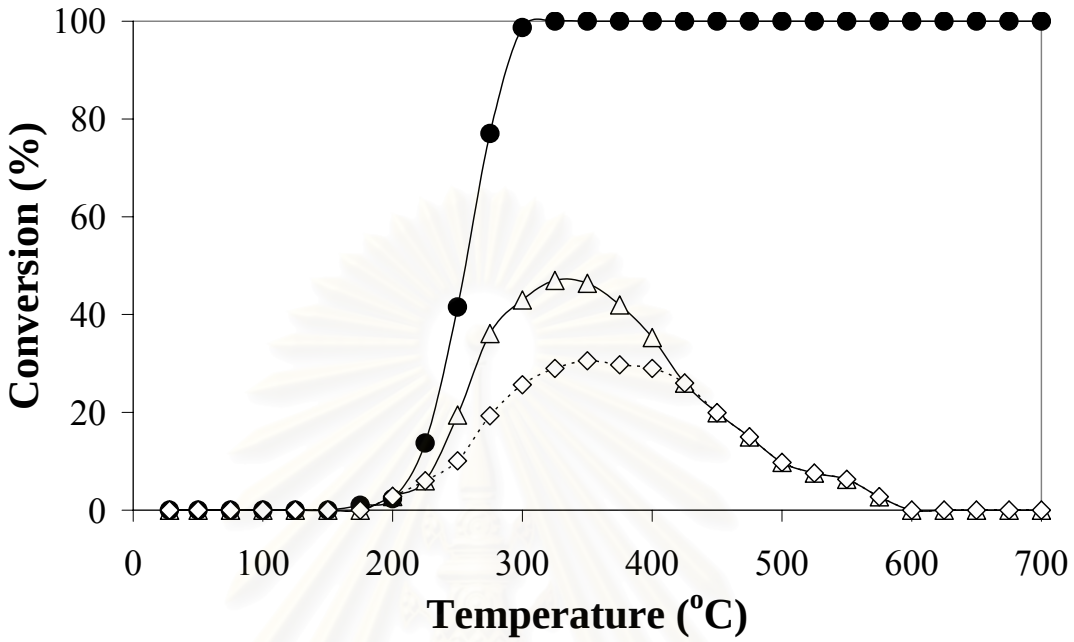

Figure 4.4 The temperature programmed reaction profiles of 10 wt% Ag/Al_2O_3 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion, (△) total NO conversion to N_2 and N_2O as well as (◇) NO conversion to N_2O.

4.2.2 The nature of surface species

In this part, temperature programmed techniques were undertaken to identify the active intermediate species and propose the possible reaction pathways in the C_3H_6-SCR of NO over Ag/Al_2O_3 catalysts. Temperature programmed techniques consist three steps containing reaction step, temperature programmed desorption (TPD) and temperature programmed oxidation (TPO). It is remarked that in the first step the surface species were produced at the constant temperature. Afterwards, the TPD was carried out to remove the adsorbed surface species. Finally, the remaining surface species were removed in the TPO step. All compositions of the effluent gases in these experiments would be expected to provide some insight into the nature of the adsorbed species on the catalyst surface. However, the features of surface species on

the catalyst surface are carefully considered because the surface species do not behave only the intermediate species but also the spectator species.

To prevent elimination of all the intermediates by O_2 during the production step of the surface species, in the TPD-TPO experiments, the surface species have to be introduced at a temperature above an onset temperature for C_3H_6 oxidation, but below the temperature at which combustion goes to completion, that is, between 325 and 550 °C for the 2 wt% Ag/Al_2O_3 and between 200 and 300 °C for the 10 wt% Ag/Al_2O_3. Because of this, the dosing temperatures of 370 °C and 210 °C in the first step of TPD-TPO experiment are used for the 2 wt% Ag/Al_2O_3 and the 10 wt% Ag/Al_2O_3, respectively.

After exposure the Ag catalysts to a gas mixture of C_3H_6, NO and O_2 at a given temperature, the C_3H_6 and NO conversion of each system is equally approximately 60%. Figures 4.5 and 4.6 show gas evolution from surface of the 2 wt% Ag/Al_2O_3 dosed with reactants (C_3H_6+NO+O_2) at 370 °C for 2 h during TPD and TPO steps, respectively. It is noted that there appears gas evolution during TPD and TPO steps, unlike zeolite- and platinum-based catalysts as reported previously elsewhere [40,41]. The surface species on Pt formulation are almost totally released during TPD step whereas those on metal ion exchange ZSM-5 are necessarily removed by the oxidant on TPO step.

These effluent gases contained CO_2, CH_4 and N_2 in the TPD step and only CO_2 and N_2 in the TPO step. Other species expected to be present such as NO, NO_2 and NH_3 were not observed in this experiment due to limitations of our analysis. Zuzaniuk et al. [37] reported production of NO_2 and NH_3 in oxidation of nitromethane and *tert*-butyl nitrite, which were assigned as models of possible intermediates. Considering the TPD profile, the effluent gases are obtained by decomposition process of some surface species, perhaps intermediates. For TPD step, as seen in Figure 4.5, a 600 °C CO_2 peak occurs at about the same temperature as a CH_4 peak. There is in addition a broad CO_2 peak appearing at approximately 400 °C coincident with a very little N_2 peak.

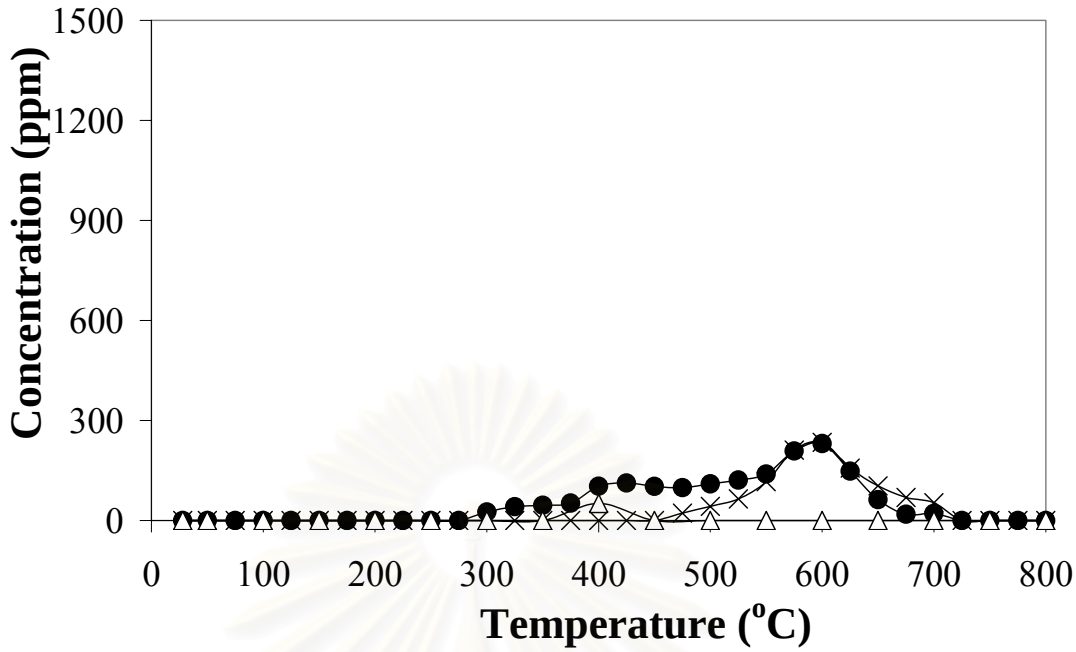

Figure 4.5 The temperature programmed desorption profiles of 2 wt% Ag/Al_2O_3 after dosing 1000 ppm C_3H_6 + 1000 ppm NO + 5% O_2 at 370°C for 2 h: (△) N_2, (●) CO_2 and (×) CH_4.

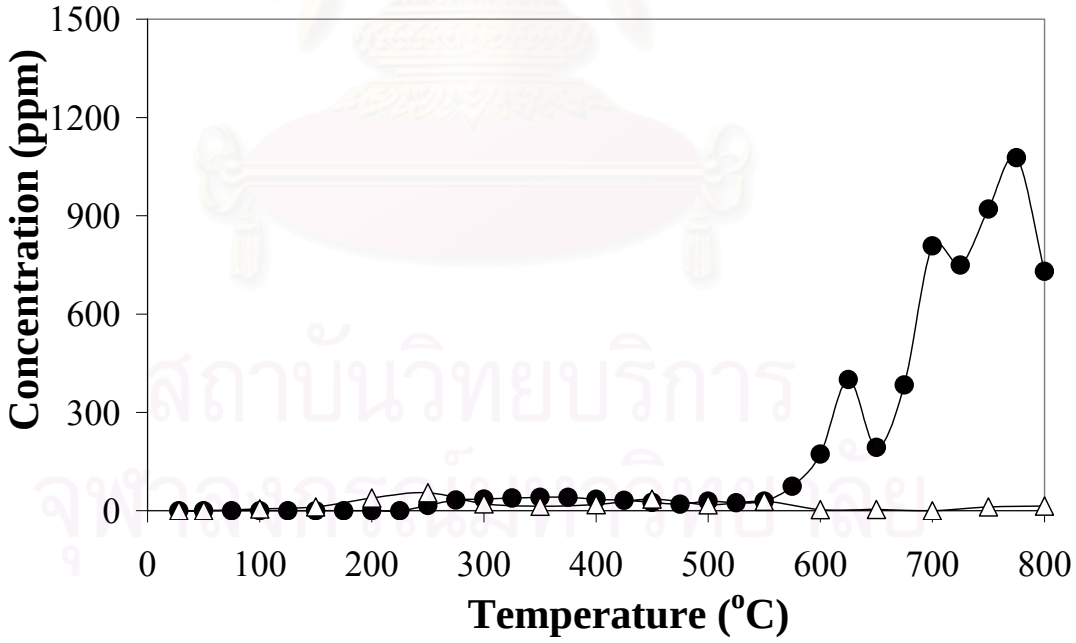

Figure 4.6 The temperature programmed oxidation profiles of 2 wt% Ag/Al_2O_3 by using 1% O_2 as the oxidizing gas after the two steps, reaction and TPD steps: (△) N_2 and (●) CO_2.

In case of TPO surface species, this profile shows oxidation characteristic of the remaining deposits. It is also reminded that these deposits cannot decompose under He atmosphere at below 800 °C. Three large CO_2 peaks are centered at 625, 700 and 775 °C. There is in addition very small signal of CO_2 and N_2 at below 500°C, but probably significant.

It is speculated that each peak should be assigned to decomposition of at least one surface species, but possibly two may be involved. However, when there is a coincidence of peaks both probably arise from the same single surface species. Deconvolution of TPD profile suggests that at least two surfaces species on catalyst surface can decompose even in an inert gas. Since their structure and composition are as yet unknown, these species are designated as S_{TPDL} and S_{TPDH}. The former species is associated with the CO_2 and N_2 peaks at about 400 °C, while the latter species appears related to the CO_2 and CH_4 peaks at 600 °C. Nitrogen is present only in the structure of S_{TPDL}. For TPD surface species, the existence of these surface species is in agreement with the observation by IR technique [78]. This results involves the observation of isocyanate (-NCO) and formate (CH_3COO-) species on Ag/Al_2O_3 in $C_3H_6+NO+O_2$ system. It was also found that surface isocyanate on Ag/Al_2O_3 disappeared distinctly when flushed with He flow at 500 °C while the removal of formate species was observed over 500 °C. This is consistent with our discovery that only S_{TPDL} can decompose under He atmosphere in the temperature range of 300-500 °C. In addition, only S_{TPDH} decompose over 600 °C. As a consequence, it could be generally admitted that the species observed at low temperature indicate the formation of $C_wH_xO_yN_z$ species resulting from the oxidation of with NO or the oxidation of the other species with NO while the species appeared at high temperature exhibit the formation of $C_xH_yO_z$ species resulting from partial oxidation of propene.

For TPO surface species, TPO profile shows at least three surfaces species being oxidized by O_2 at high temperature. To accommodate for discussion, we combine the three species to be only one group and designate a group of these species as S_{TPOH}.

Because of the results of activity mentioned above, nature of the surface species on the high-loading Ag catalyst was additionally studied in order to fulfill our information. Gas evolutions during TPD and TPO experiments of the 10 wt% Ag/Al_2O_3 exposed to a gas mixture of C_3H_6, NO and O_2 at 210 °C for 2 h are shown in Figures 4.7 and 4.8, respectively.

Clearly, there are some differences in TPD-TPO patterns compared to the low-loading Ag catalyst. The TPD surface species on the 10 wt% Ag/Al_2O_3 are much more produced than that on the 2 wt% Ag/Al_2O_3. Considering gas evolution in the TPD profiles (see Figure 4.7), there are two CO_2 peaks at 325 and 575 °C as well as a shoulder at ca. 450 °C while N_2 and CH_4 show only one peak at 275 and 575 °C, respectively. The 575 °C carbon-containing species (coincidence of CO_2 and CH_4 peaks) seems to show the same characteristic of S_{TPDH} on low-loading silver but much more production. The N_2 peak is a 125 °C shift from the experiment of the low-loading silver. This is relative with a shift of the 325 °C CO_2 peak although just 75 °C of the maximum CO_2 position is shifted. However, we that these N_2 and CO_2 decompose from the same sort of surface species. Two possible reasons are pronounced to explain the shift of the N_2 and CO_2 peaks. First, these species are actually S_{TPDL} but either their decomposition behavior or structural composition is changed. An example is change of the decomposition temperature of isocyanate species if this species occurs on the different catalyst surface. Over 2 wt% Ag/Al_2O_3 the isocyanate species disappeared completely at about 500 °C [78] while it vanished definitely at just 350 °C on 0.8 wt% Pt/Al_2O_3 [79]. The second reason is occurrence of new surface species definitely independent on S_{TPDL}. Iglesias et al. [77] reported about the different of surface species for high and low silver loading. That significant difference was identification of cyanide species for the former on high silver loading, appearing initially at 300°C. We assign the species that contain with N and decompose during TPD step as $S_{TPDL.}$ This is relative with a shift of operating temperature that contain with N-containing compound can decompose to produce N_2 and CO_2 at low temperature when compare with TPD surface of low Ag loading. However, we found that the only shoulder of CO_2 for high loading appear at 400°C at which was the same temperature of S_{TPDL} decomposition for low loading. Some literature [78] reported about the disintegration of aldehyde species that the

decomposition of this occurs at 425°C. We designate a species as S_{TPDM}. From the previous work [40,42], two relatively peaks at 325 and 525°C are also observed. There are two CO_2 peaks at 350 and 500°C. These species are designated as $C_xH_yO_zN_w$ and $(C_lH_mO_n)_{HT,}$ respectively. The positions of both species are coincident with the two CO_2 peaks of S_{TPDL} and S_{TPDH} species appearing in the TPD profile for the dosing reactants gases.

For TPO step, both different and similar surface species loading Ag were observed as shown in Fig.4.8. The surface species were oxidized and released both low and high temperature. At low temperature, the surface species is more produced than that appears in 2 wt% silver. We assign these species as S_{TPOL}.

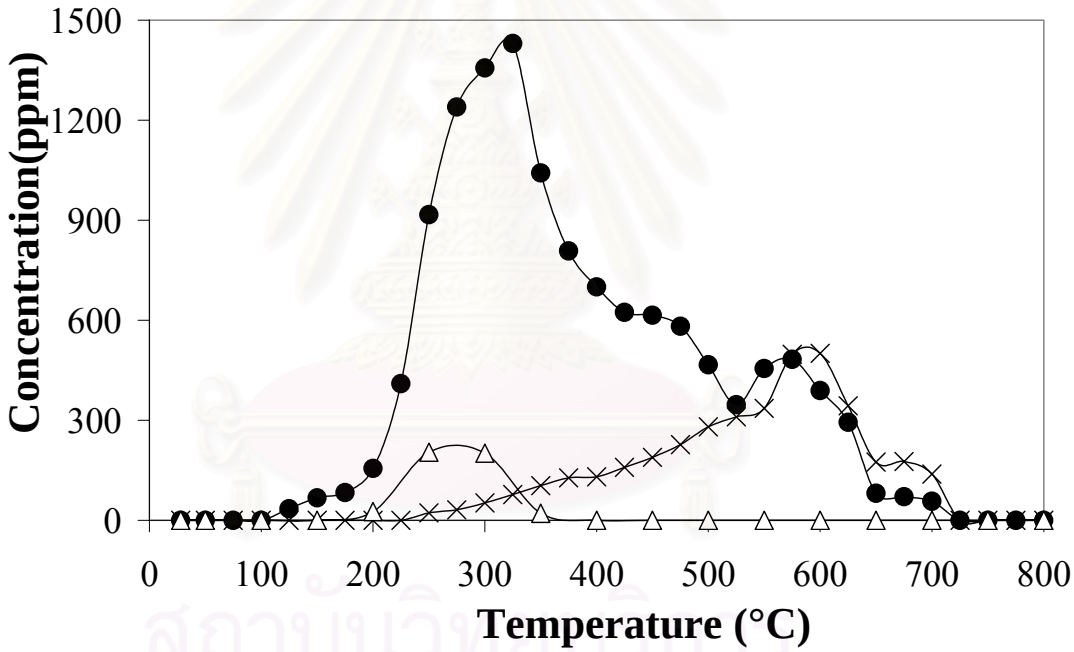

Figure 4.7 The temperature programmed desorption profiles of 10 wt% Ag/Al_2O_3 after dosing 1000 ppm C_3H_6 + 1000 ppm NO + 5% O_2 at 210°C for 2 h: (△) N_2, (●) CO_2 and (×) CH_4.

Certainly, the surface species may possible play a role to be either the intermediate species or the spectator species. For example, nitrite (-CN) and isocyante species were proposed as the intermediates for the selective catalytic reduction of NO by hydrocarbon over Ag/Al_2O_3 [65]. In addition, there is some work suggested that acetates were the catalytic intermediate for the selective catalytic

reduction of NO by n-hexane over Ag/Al_2O_3 while nitrate species exhibited the behavior of spectator in this reaction [64]. Therefore, the surface species released in TPD and TPO steps need to be tested the reactivity with reactant under reaction condition. The species, which can be decomposing or oxidized at a relative temperature, is possible to be an intermediate. Hence, the reactivity of surface species that appear in TPD and TPO steps with oxidizing reactant gases was studied. The reactivity test was conducted by using TPO technique without or with TPD step. Before the reactivity tests, the surface species were produced by dosing a gases mixture of C_3H_6+NO+O_2 at 370 and 210 for 2% and 10% Ag/Al_2O_3, respectively. Temperature programmed oxidation with oxidizing reactant gases such as O_2 and NO+O_2 was used to test the reactivity.

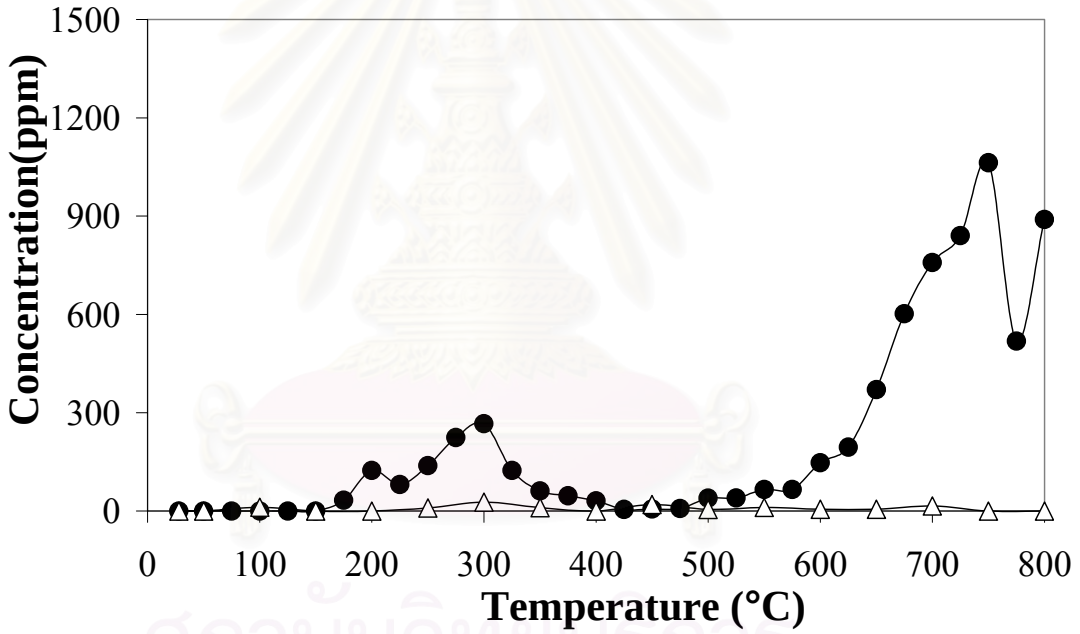

Figure 4.8 The temperature programmed oxidation profiles of 10 wt% Ag/Al_2O_3 by using 1% O_2 as the oxidizing gas after the two steps, reaction and TPD steps: (△) N_2 and (●) CO_2.

To study the characteristics of TPD surface species, the TPO by O_2 without TPD technique was made. Figure 4.9 shows the traces of outlet gases obtained from the oxidation of surface species by O_2 over 2% Ag/Al_2O_3 catalyst after exposed to C_3H_6+NO+O_2. The effluent gases contain CO_2 and N_2. It is found that the position of CO_2 peak addressed as S_{TPDL} was unaffected with introducing O_2 as oxidizing gases

while the CO_2 and CH_4 peak addressed as S_{TPDH} disappeared. We speculate that S_{TPDH} should be oxidized by O_2 and transformed to be CO_2 and N_2 centered at 425°C. This result indicates that S_{TPDL} species can decompose even in excess oxygen at the same temperature where decompose under helium atmosphere. On the other hand, S_{TPDH} is easily oxidized by O_2. The similar result was reported by Shimizu et al. [64]. They found that

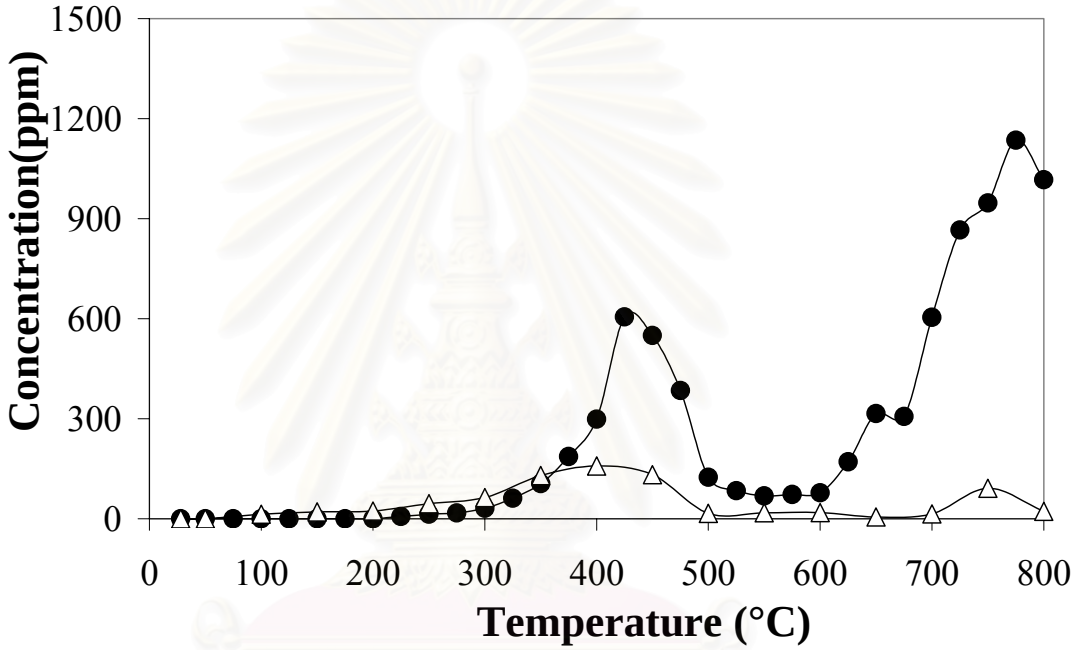

Figure 4.9 The temperature programmed oxidation profiles of 2 wt% Ag/Al_2O_3 by using 1% O_2 as the oxidizing gas after dosing 1000 ppm NO + 1000 ppm C_3H_6 + 5% O_2 at 370°C for 2 h: (△) N_2 and (●) CO_2.

Figures 4.10 and 4.11 show the effluent gases obtained from the oxidation of surface species by $NO+O_2$ without and with TPD step over 2% Ag/Al_2O_3 catalyst after exposed to $C_3H_6+NO+O_2$. When the oxidizing gas is changed to $NO+O_2$, the reactivity of S_{TPDH} and S_{TPOH} surface species was observed both reactivity tests. S_{TPDH} was oxidized with $NO+O_2$ to produce CO_2 at the lower temperature while CO_2 at high temperature disappeared. From the above results, it indicates that the surface species decomposing at high temperature addressed as S_{TPDH} species is easily removed by both O_2 and $NO+O_2$.

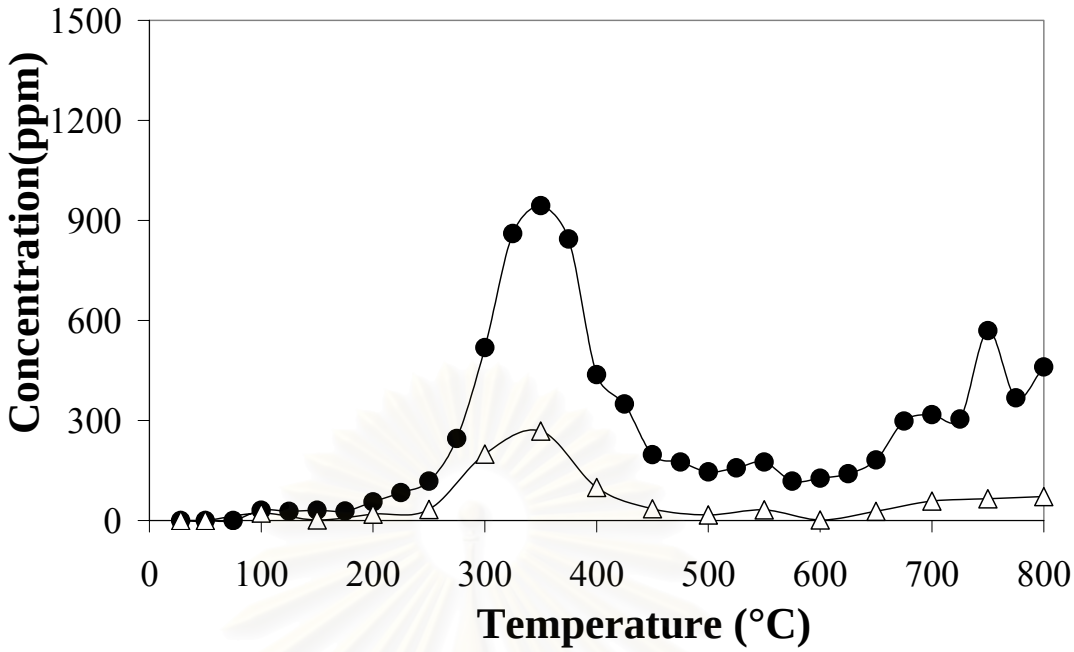

Figure 4.10 The temperature programmed oxidation profiles of 2 wt% Ag/Al_2O_3 by using 1% O_2+1000 ppm. NO without TPD as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 370°C for 2 h: (△) N_2 and (●) CO_2.

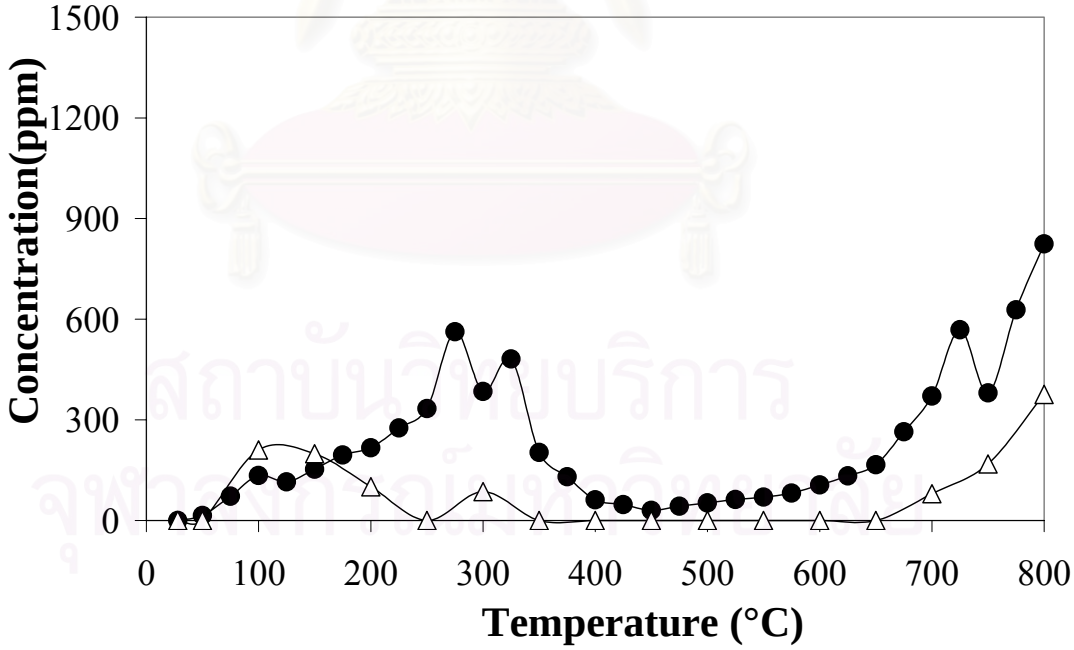

Figure 4.11 The temperature programmed oxidation profiles of 2 wt% Ag/Al_2O_3 by using 1% O_2+1000 ppm. NO as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 370°C for 2 h: (△) N_2 and (●) CO_2.

For S_{TPOH} species, a large amount CO_2 released at low temperature and diappearence of the CO_2 peak at high temperature imply that this species are partially reactive with $NO+O_2$. However, the remainder of CO_2 peak at high temperature was observed as seen in Figures 4.10 and 4.11. It is revealed that some of S_{TPOH} was not reactive with $NO+O_2$. It was remarked that after TPD technique S_{TPOH} species was oxidized by $NO+O_2$ and appeared at the lower temperature where it was removed under $NO+O_2$ without TPD. This indicates that the presence of the TPD surface species may be inhibit the reaction of TPO surface species.

The reactivity of S_{TPOH} is in agreement with the results of Shimizu et al. [30] and Meunier et al [34]. Shimizu et al. reported regarding the reactivity of acetate, which is produced via the partial oxidation hydrocarbon that the acetate, which was stable in O_2 atmosphere, was reactive in $NO+O_2$. In addition, Meunier et al. suggested that nitrate species could still be observed over 600ºC. It was remarked that the S_{TPOH} species after TPD step were readily reactive with $NO+O_2$ and removed at the lower temperature where they were removed under $NO+O_2$ without TPD. This indicates that the TPD species may inhibit the reaction of TPO surface species because the TPD species are much more easily reacted with oxidant gases than the TPO species.

Unfortunately, we can not determine from these experiments that weather S_{TPOL} is reacted with $NO+O_2$ or not. The reactivity with reactants gas was not observed because the little amount of this species was released in TPO step at low temperature. From these results, the reactivity tests of surface species over 10% Ag/Al_2O_3 were made to give the more information confirmed.

In case of $10\%Ag/Al_2O_3$, the concentrations of carbon dioxide and nitrogen containing compounds removed during the oxidation steps by using $NO+O_2$ as the oxidizing gases without and with TPD step are exhibited in Figures 4.12 and 4.13, respectively. The reactivity of surface species illustrated some similar results with $2\%Ag/Al_2O_3$.

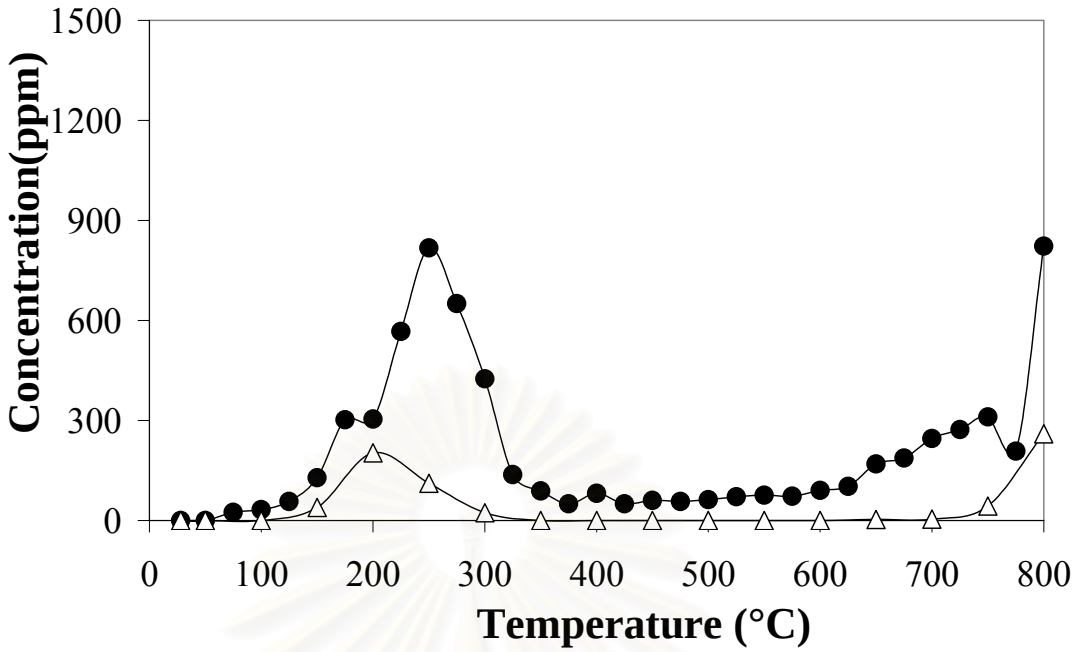

Figure 4.12 The temperature programmed oxidation profiles of 10 wt% Ag/Al_2O_3 by using 1% O_2+1000 ppm. NO TPD as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 210°C for 2 h: (△) N_2 and (●) CO_2.

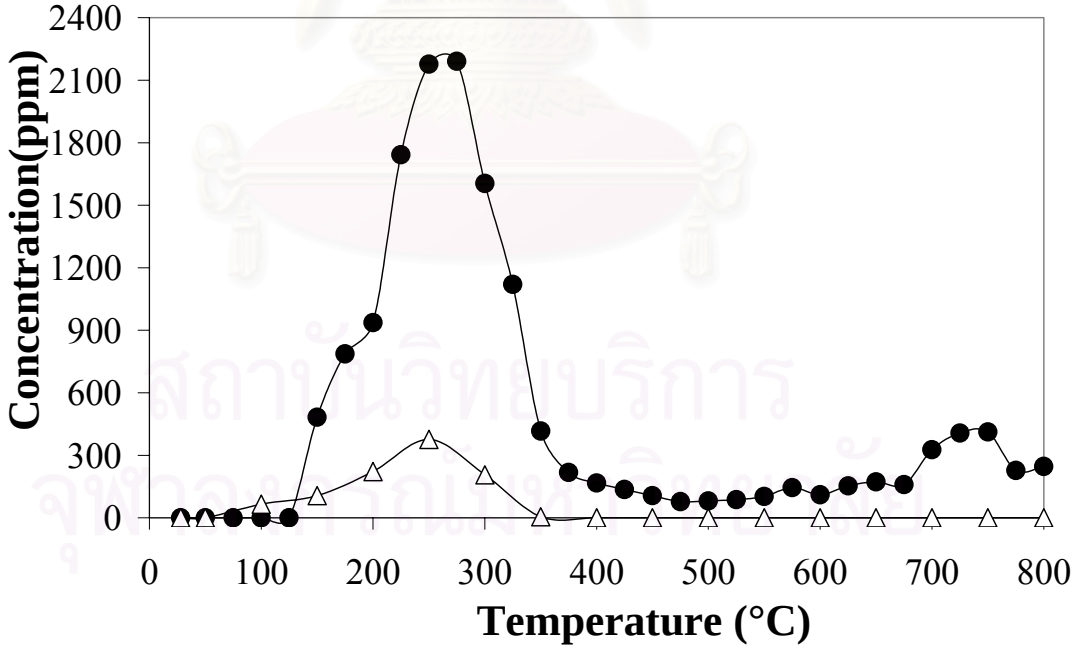

Figure 4.13 The temperature programmed oxidation profiles of 10 wt% Ag/Al_2O_3 by using 1% O_2+1000 ppm. NO as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 210°C for 2 h: (△) N_2 and (●) CO_2.

Considering the reactivity of surface species at moderate (S_{TPDM}) and high temperature (both S_{TPDH} and S_{TPOH} species), when $NO+O_2$ were used as the oxizing gases, the vanishing of carbon dioxide peak appeared both TPD profile (Figure 4.7) and TPO profile (Figure 4.8) was observed while a large amount of carbon dioxide peak much more produced at lower temperature (250°C) as shown in Figure 4.13, which is different from low loading silver.

From the above results described in section 4.2.2, the observation of five types of surface species indicates the complication in formation of surface species. We can speculate that all surface species involve the formation of N_2 or CO_2 in HC-SCR on Ag/Al_2O_3 because these species are reacted with reactant gases in reaction temperature. However, there are only two surface species, S_{TPDL} and S_{TPOH}, regarding the production of N_2. Considering the behavior of two surface species, S_{TPDL} species can decompose or desorb while S_{TPOH} is oxidized with $NO+O_2$ to produce N_2. And the temperature of decomposition or oxidation for both species can shift together with the reaction temperature. Therefore, it is predicted that there are at least two main reaction pathways dependent on characteristic of surface species and temperature of reaction. The parallel reaction mechanisms are decomposition and oxidation of surface species as shown in equation 4.1 as well as 4.2, respectively.

$$S_{TPDL} \rightarrow CO_2 + N_2 \qquad (4.1)$$

$$S_{TPOH} + NO + O_2 \text{ or } O_2 \rightarrow CO_2 + N_2 \qquad (4.2)$$

First, S_{TPDL} species decomposed or desorbed to produce nitrogen and carbon dioxide. This reaction occurs at moderate temperature. Second, the oxidations of S_{TPOH} species with $NO+O_2$ and O_2 are performed at low temperature while the remainder of S_{TPOH} species is oxidized with $NO+O_2$ to produce nitrogen at high temperature.

4.2.3 The nature study by using physical mixture of Ag/SiO_2 and Al_2O_3

Although the characteristic of surface species was investigated using the reactivity tests, but this methods does not show the appeared position of surface species that occur on metal active site or metal-support interface or support active site. In this section, the study of surface species was carried out on a physical mixture of Ag/SiO_2 and Al_2O_3 on the assumption that SiO_2 is not active for the SCR reaction [76]. Before the study by using physical mixture, the activities and selectivities of these mixture systems are necessarily tested to consider the NO and C_3H_6 conversions. If the similar patterns of TPR data with Ag/Al_2O_3 are observed, the mixture of Ag/SiO_2 and Al_2O_3 will be used to probe the behavior of surface species. Figure 4.15 shows temperature programmed reaction profiles of 2% Ag/SiO_2 and Al_2O_3. The conversions result in two parts separately. First, the maximum yield of nitrogen slightly decrease from 35% at 250 °C while the C_3H_6 conversion rises together with NO conversion and reaches maximum at 300°C. This maximum conversion is 95%. The other, both NO and C_3H_6 conversions increase again after the reductive conversion has been observed at 350°C. The overall NO reduction conversion reaches a sharp maximum of approximately 70% at 500°C. The peak for reduction to N_2O occurs about 200-350 and 450-550°C.

The TPR profile over 10% Ag/SiO_2 and Al_2O_3 is shown in Figure 4.16. Similar tendency with 2% silver is observed. The overall NO reduction conversion reaches a sharp maximum of approximately 10% and 50% at 200 and 500°C, respectively. In term of CO_2, the first CO_2 peak appears at 200°C and reaches a constant maximum at 95% until the temperature increase to 350°C. The complete combustion of second CO_2 peak occurs at 500°C.

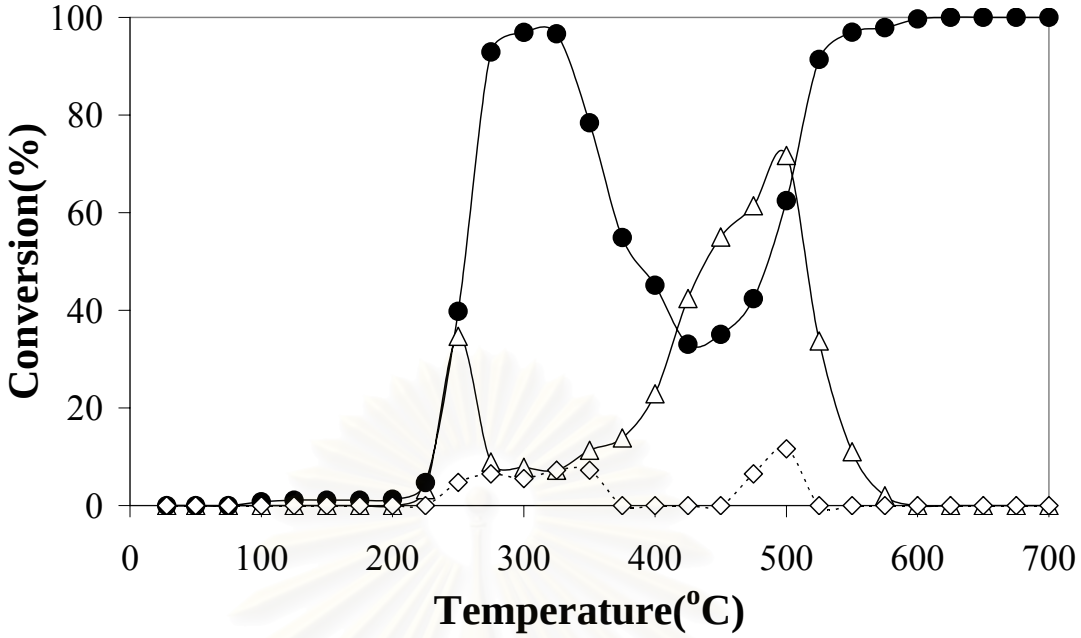

Figure 4.14 The temperature programmed reaction profiles of 2 wt% Ag/SiO_2 and Al_2O_3 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion, (△) NO conversion and (◇) NO conversion to N_2O.

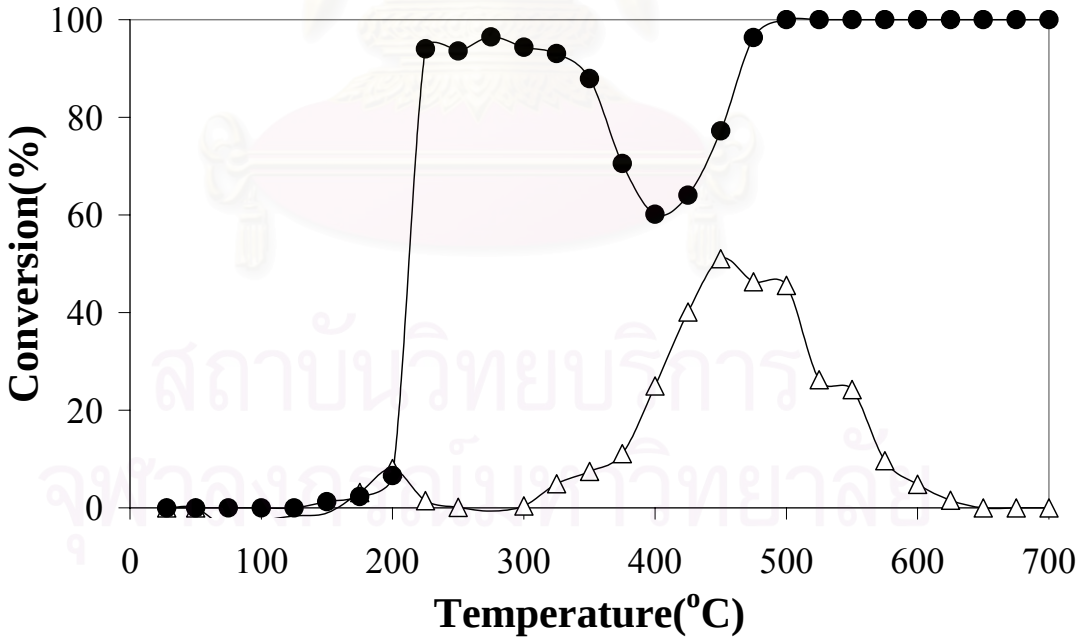

Figure.4.15 The temperature programmed reaction profiles of 10 wt% Ag/SiO_2 and Al_2O_3 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion and (△) NO conversion

The comparisons of TPR results between Ag/Al_2O_3 and the physical mixtures method show the different profile. The profile of TPR over Ag/Al_2O_3 appears one while the physical mixtures show two characteristic. Hence, these methods not use to investigate the behavior of surface species. However, from both methods, the significant differentia between low and high silver loading is observed. The NO conversion for low silver loading reaches higher maximum than high silver loading. It indicates that the low silver loading promote NO reduction. In contrast, CO_2 from combustion over high loading much more produce than low loading silver and onset temperature over high loading shift to lower temperature. This result demonstrates that high loading is promoter for HC combustion. This behavior is in agreement with the results reported several work [36, 76].

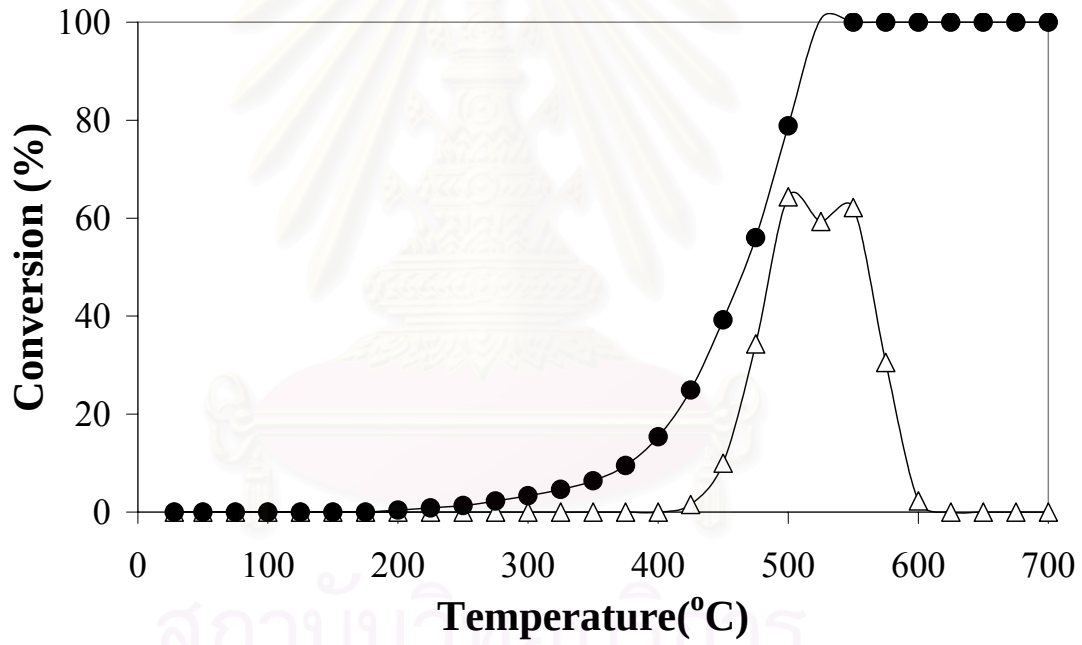

Figure.4.16 The temperature programmed reaction profiles of Al_2O_3 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion and (△) NO conversion

In addition, we found that at high temperature (400-600°C) the NO conversion profile of SCR over physical mixture show the similar activity pattern with Al_2O_3 as shown in Figure 4.16. The NO conversion over Al_2O_3 catalyst appeared at temperature range from 350 to 600 °C. Another NO conversion at low temperature may occur over Ag/SiO_2. To confirm this assumption, TPR of Ag/SiO_2 was made and

shown in Figure 4.17. It is noted that both NO and C_3H_6 conversion appeared approximately 200-300°C show only effect of silver.

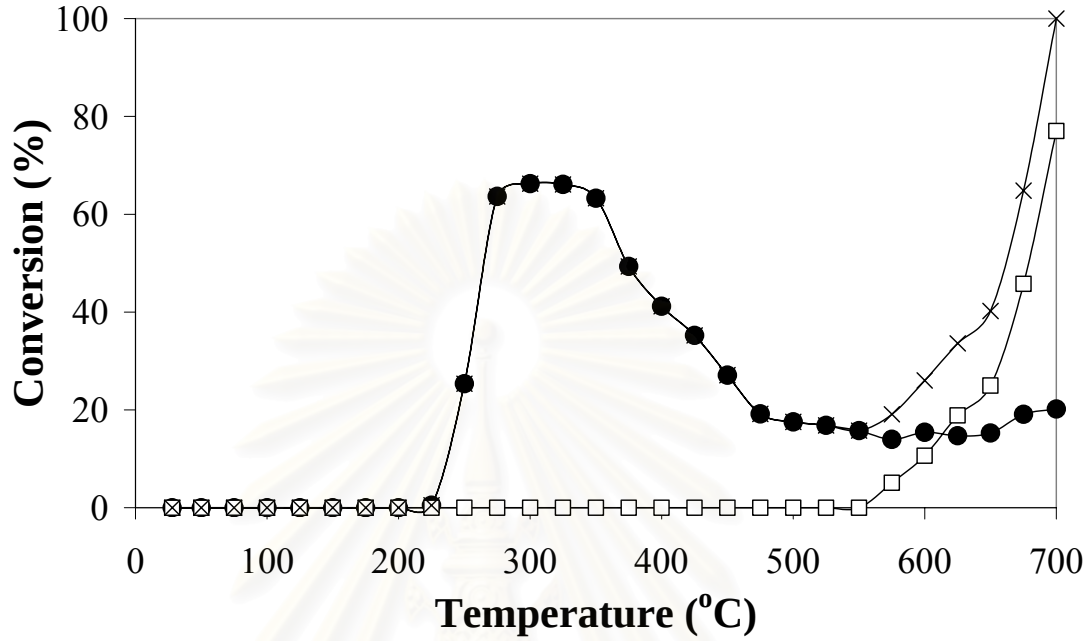

Figure 4.17 The temperature programmed reaction profiles of 2 wt% Ag/SiO_2 for the selective catalytic reduction of NO by C_3H_6 under excess oxygen: (●) C_3H_6 conversion to CO_2, (x) total C_3H_6 conversion and (□) C_3H_6 conversion to CO.

From the above result, temperature programmed technique was used to study the nature of surface species over Ag/SiO_2 catalyst to classify the occurred species over silver active site. The surface species have to be produced at a temperature 370 °C in the first step of TPD-TPO experiment. After dosing steps, the surface species occur both TPD and TPO steps. Figures 4.17 and 4.18 show gas evolution from surface of the 2 wt% Ag/SiO_2 dosed with reactants (C_3H_6+NO+O_2) at 370 °C for 2 h during TPD and TPO steps, respectively. The released gases during TPD step consist CH_4 and a little CO_2 while no N_2 was detected. A little CO_2 group appears at 350°C while small CH_4 is observed at 750°C. From this result, it possible that the adsorbed HC species crack and produce CH_4 at high temperature. Considering the TPO profile, the effluent gases are obtained by decomposition process of some surface species, perhaps intermediates. Above 600 °C three CO_2 peak occurs at the same temperature as oxidation of S_{TPOH} species over Ag/Al_2O_3. From the corresponding of this species.

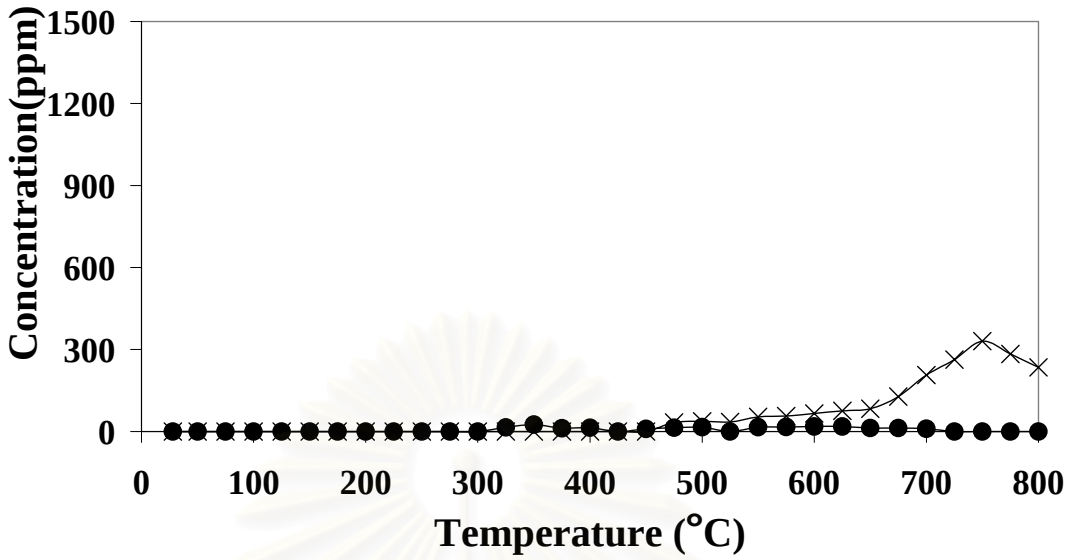

Figure 4.18 The temperature programmed desorption profiles of 2 wt% Ag/SiO_2 and Al_2O_3 after dosing 1000 ppm C_3H_6 + 1000 ppm NO + 5% O_2 at 370°C for 2 h

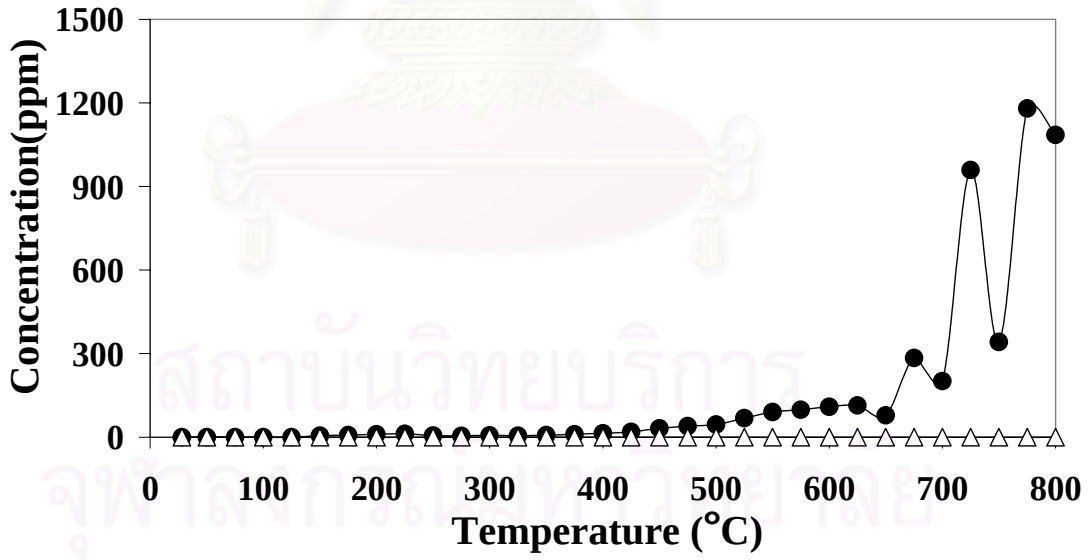

Figure 4.19 The temperature programmed oxidation profiles of 2 wt% Ag/SiO_2 and Al_2O_3 by using 1% O_2 as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 370°C for 2 h

both Ag/SiO_2 and Ag/Al_2O_3, the characteristic study of this species over Ag/SiO_2 probably exhibit the behavior of this species over Ag/Al_2O_3. Hence, the reactivity of S_{TPOH} species over Ag/SiO_2 was made

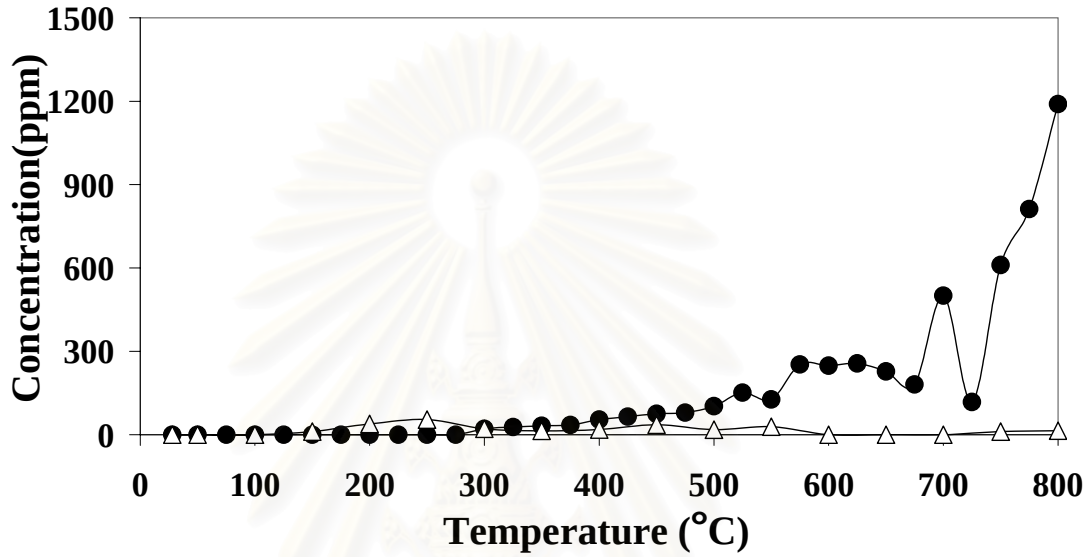

Figure 4.20 The temperature programmed oxidation profiles of 2 wt% Ag/SiO_2 and Al_2O_3 by using $NO+O_2$ as the oxidizing gas after dosing 1000 ppm C_3H_6 + 5% O_2 at 370°C for 2 h.

The behavior of surface species over Ag/SiO_2 was tested by using the temperature programmed oxidation with $NO+O_2$ without TPD step. The reactivity of surface species shows in Figure 4.20. The observed groups of CO_2 peak above 500°C not shift to the lower temperature during the changing of oxidant gases. In contrast, the S_{TPOH} over Ag/Al_2O_3 reacted with $NO+O_2$ at low temperature. It may be possible that the adsorbed species on Ag/SiO_2 occurred only on silver metal active sites and then blocked these active sites, which used to form the adsorbed species while adsorbed species on Ag/Al_2O_3 appeared both metal and support active sites.

Table 4.1 Metal Active Sites Measurement of Silver

Sample	Metal Active Site
2 % Ag/Al_2O_3	$2.50x10^{19}$
2 % Ag/Al_2O_3 after pretreat with time on stream and TPD	$1.58x10^{19}$
2 % Ag/SiO_2	$1.87x10^{19}$
2 % Ag/SiO_2 after pretreat with time on stream and TPD	0

To confirm this result, the measured metal active site by using N_2O adsorption method was made. The metal active site of silver is shown in Table 4.1. After pretreated with reaction step and released TPD species, the remainder of silver active site over Ag/Al_2O_3 is $1.58x10^{19}$ while no silver active site remains for Ag/SiO_2 systems. It confirm that the formation of surface species over Ag/Al_2O_3 occur on alumina active sites while the adsorbed surface species over Ag/SiO_2 was formed on only silver active site. It is agreement with the results reported by Bio et al.[20]. They found that the surface species first adsorbed on silver active site and reacted with alumina active site to from the surface species on alumina active sites, then the surface species on alumina active sites was reacted with oxidizing gases to form N_2.

From the observation regarding the reactivity test of S_{TPOH}, this species first adsorbed on silver active sites and can react with $NO+O_2$ to produce carbon dioxide and nitrogen at low temperature, which is the same temperature of low temperature surface species appearing. Moreover, no S_{TPDL} species appeared in case of Ag/SiO_2. Therefore, it may be possible that the other surface species were produced from the reaction of S_{TPOH} surface species with reactant gases. Shimizu et al. [30] found that partially oxidized hydrocarbon species, such as the acteate, can reduce nitrate to N_2 via N-containing organic species, Ag^+-NCO and –CN adspecies. From this result, the experimental was performed by using the reaction with $NO+O_2$ of S_{TPOH} species over $10\%Ag/Al_2O_3$. The S_{TPOH} species was reacted with $NO+O_2+C_3H_6$ for 30 s at 210°C to form the new surface species which was investigated by using TPD step.

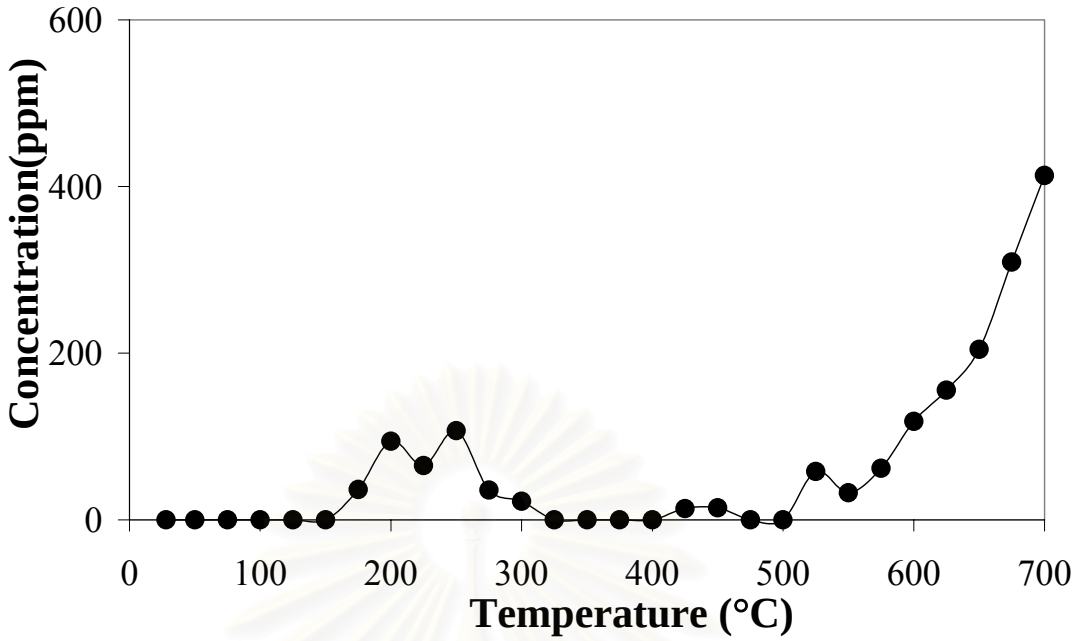

Figure 4.21 The temperature programmed desorption profiles of S_{TPOH} surface species over 10 wt% Ag/Al_2O_3 after dosing 1% O_2 + 1000 ppm NO at 210°C for 30 s:(●) CO_2.

Figure 4.21 shows the effluent gas from temperature programmed desorption S_{TPOH} species over 10% Ag/Al_2O_3 after expose to1% O_2 + 1000 ppm NO. The effluent gas consist carbon dioxide and no nitrogen was detected. The carbon dioxide appears both low temperature and high temperature which are close to the temperature of desorbed TPD species. .

However, from above result, the appeared TPD subsurface species may occur from the reaction of TPO surface species with oxidizing gases. Therefore, the other reaction mechanism is the oxidation of TPO surface species (S_{TPOH}) with oxidizing gases to produce the other surface species. It is noted that in fact, the latter reaction mechanism may hardly occur on Ag/Al_2O_3 due to its activity being preceded at low operating temperature in real condition.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

In this research, the reaction mechanism of the selective catalytic reduction of NO by hydrocarbon over Ag/Al_2O_3 catalyst under lean-burn condition is proposed via the investigation of surface species produced on the catalyst surface. The conclusions of these results are summarized as follows:

1. The different activity between low and high silver is observed. Low silver loading promotes the NO reduction at high temperature while high silver loading shows the activity at low temperature.

2. There are five surface species, $S_{TPDL,}$ $S_{TPDH,}$ $S_{TPOL,}$ S_{TPOM} as well as S_{TPOH}, observed both TPD and TPO step. The conclusions of the reactivity of surface species to various oxidizing gases shown in table 5.1.

Table 5.1 the reactivity of surface species with oxidizing gases

	S_{TPDL}	S_{TPDH}	S_{TPOL}	S_{TPOM}	S_{TPOH}
O_2	-	+	+	+	+
$NO+O_2$	-	+	n/a	+	+

3. The reaction mechanisms for the production of N_2 over Ag/Al_2O_3 consists two main pathways including the decomposition of S_{TPDL} surface species and the oxidation of S_{TPOH}.

4. From the reactivity study of surface species over Ag/Al_2O_3 and Ag/SiO_2 found that the S_{TPOH} surface species primary occurs on metal active sites. After that, this species can move to alumina active site and then reacted with $NO+O_2$ to form S_{TPDL} species.

From this work, the recommendations for further study can be as follows:

1. To confirm the proposed mechanism for C_3H_6+NO+O_2 reaction, the other techniques should be simultaneously used.

2. To employ extensively the investigation of surface species by an experimental set of three continuous steps for the prediction of reaction mechanism, other reactions should be tested, especially the reaction involving the ambiguous mechanism.

3. To develop the catalytic performance of Ag/Al_2O_3 catalyst, the detailed information about the effect of metal particle size should be profoundly studied.

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APPENDICES

APPENDIX A

SPECIFICATION OF ALUMINA SUPPORT (Al_2O_3) TYPE NKH-3

Table A.1 Chemical composition of alumina support type NKH-3

Chemical Composition	Weight percent
Al_2O_3	60-70
SiO_2	30-35
Fe_2O_3	0.3-0.5
TiO_2	0.5-0.7
CaO	0.1-0.2
MgO	0.2-0.4
Na_2O	0.3-0.4
K_2O	0.2-0.3
$ZrO_2 + HfO_2$	0.03-0.04

Table A.2 Physical properties of alumina support type NKH-3

Physical properties	
Bulk Density (g/ml)	1.3-1.5
Apparent Specific Gravity	3.1-3.3
Packing Density (lb/ft^3)	20-25
Pore Volume (ml/g)	1.0-1.3
Surface Area (m^2/g)	340-350

APPENDIX B

CALIBRATION CURVES

The thermal conductivity detectors (TCD) independently connected with two gas chromatographs (SHIMADZU GC-8ATP and SHIMADZU GC-8AIT) were used to analyze the concentration of the sampling gases in the catalytic activity test and an experimental set for studying the nature of surface species. The calibration curves of oxygen, nitrogen and carbon monoxide are obtained from TCD of GC 8ATP whereas those of oxygen, methane, carbon dioxide, nitrous oxide, propene, propane and sulfur dioxide are obtained from TCD of GC 8AIT. It is noted that the operating condition of gas chromatograph for making the calibration curves is maintained to be similar to that for testing the reaction. These calibration curves are given in Figures B.1-B.10.

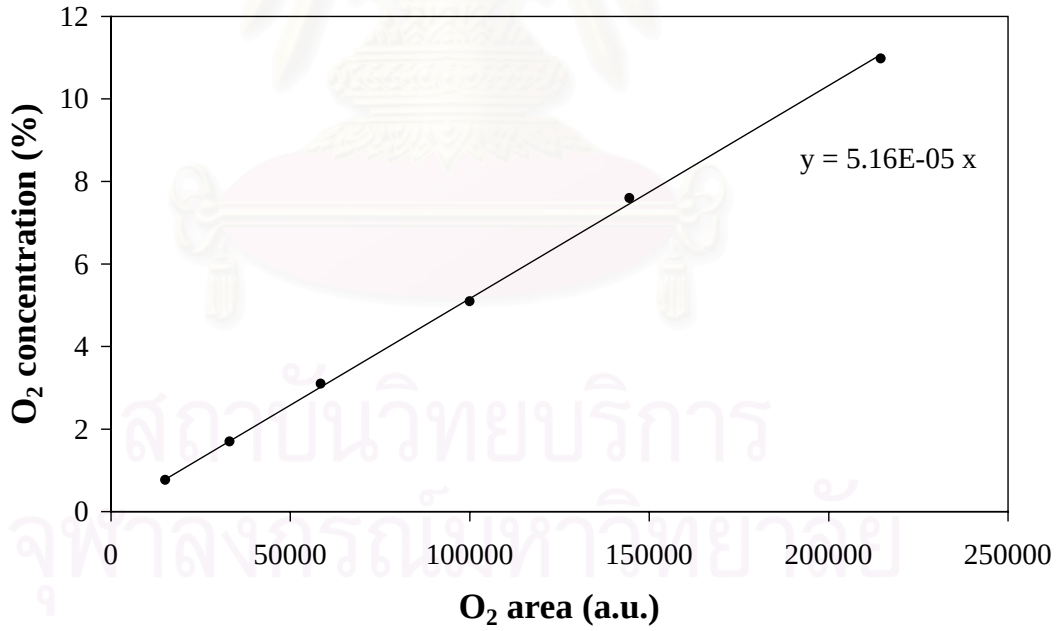

Figure B.1 The calibration curve of oxygen from TCD of GC 8ATP

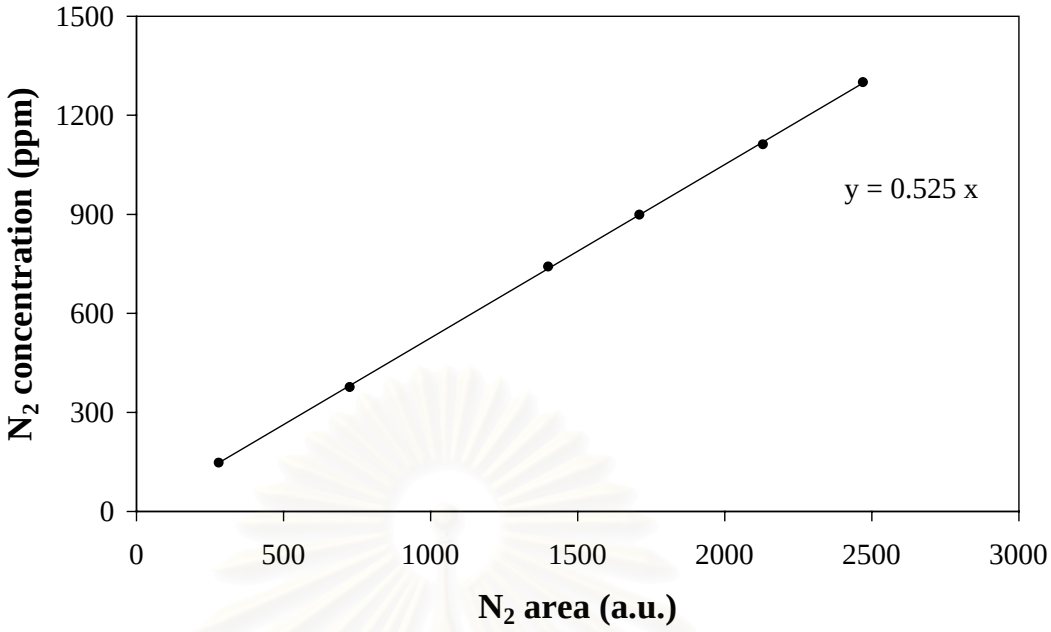

Figure B.2 The calibration curve of nitrogen

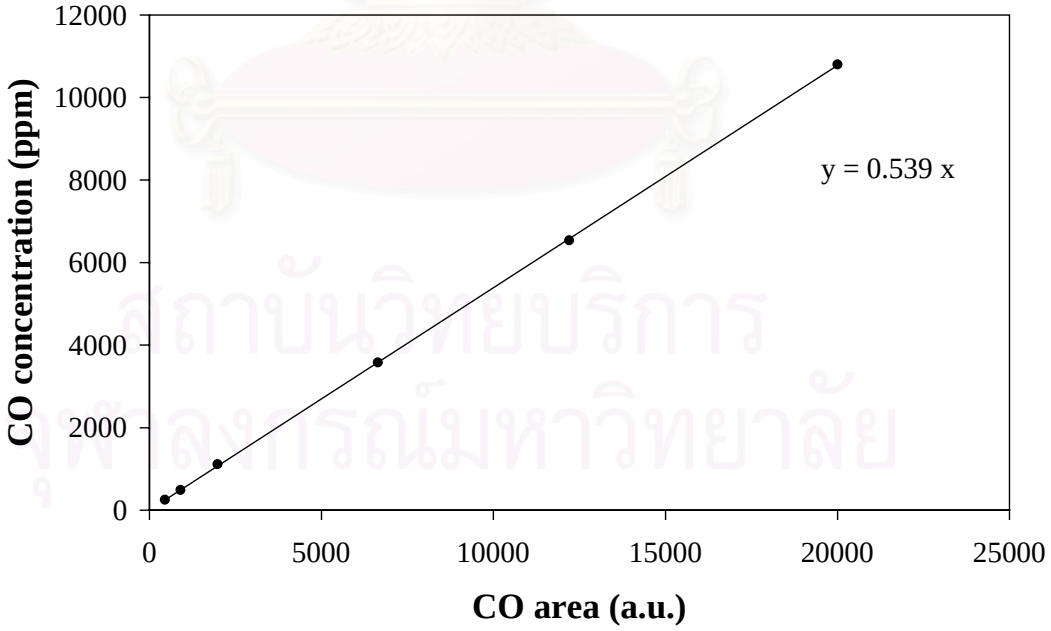

Figure B.3 The calibration curve of carbon monoxide

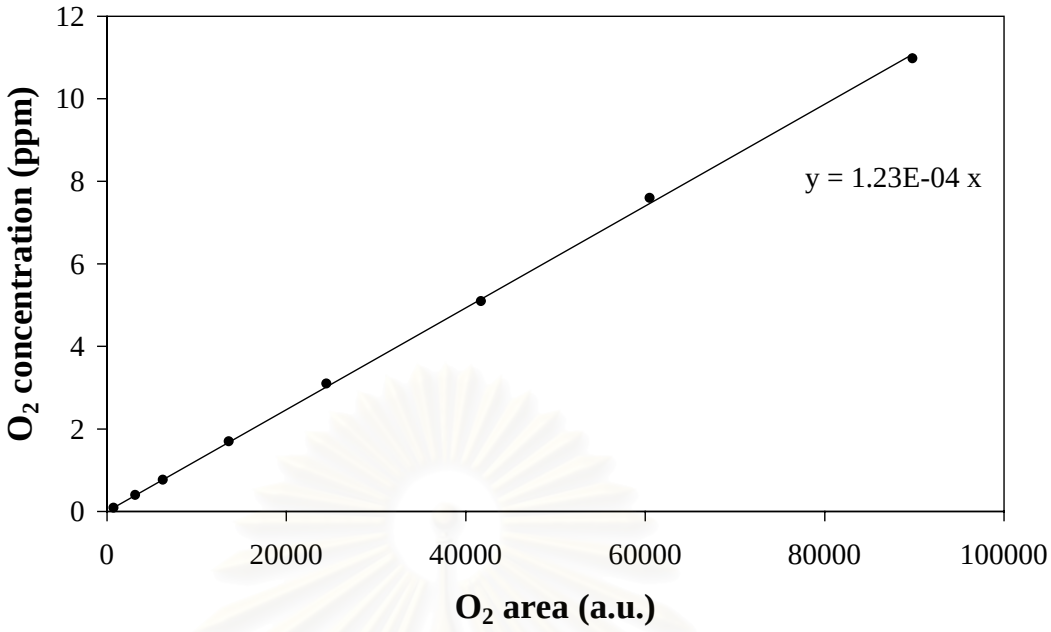

Figure B.4 The calibration curve of oxygen from TCD of GC 8AIT

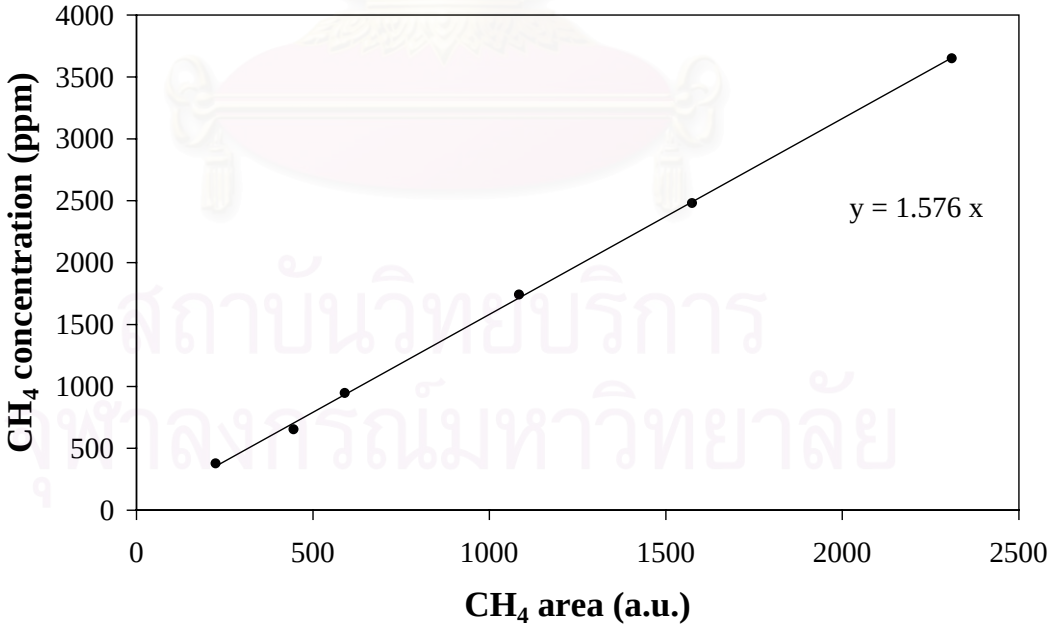

Figure B.5 The calibration curve of methane

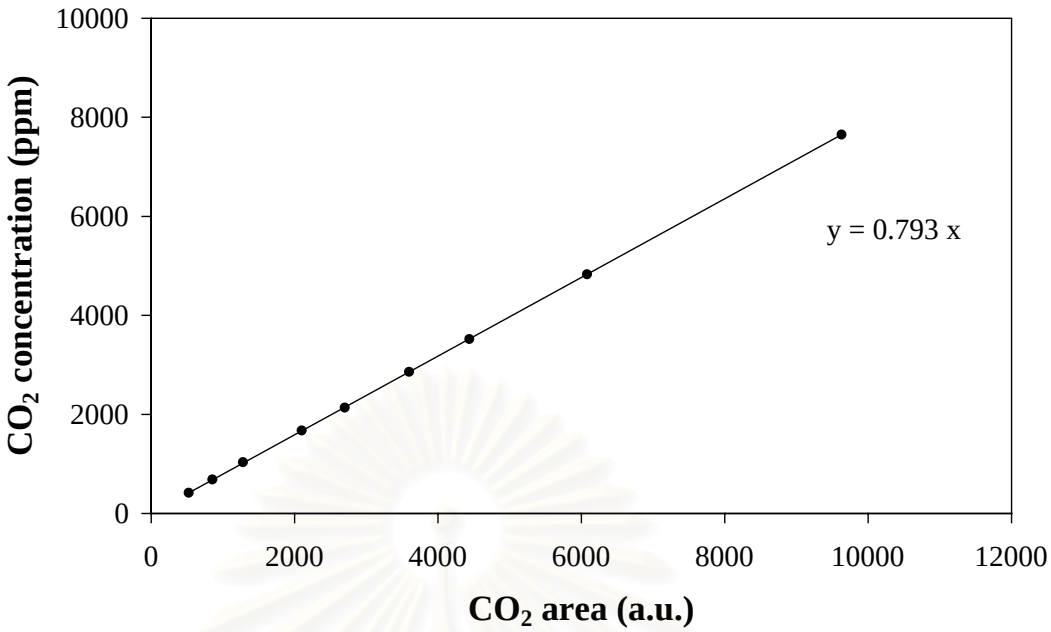

Figure B.6 The calibration curve of carbon dioxide

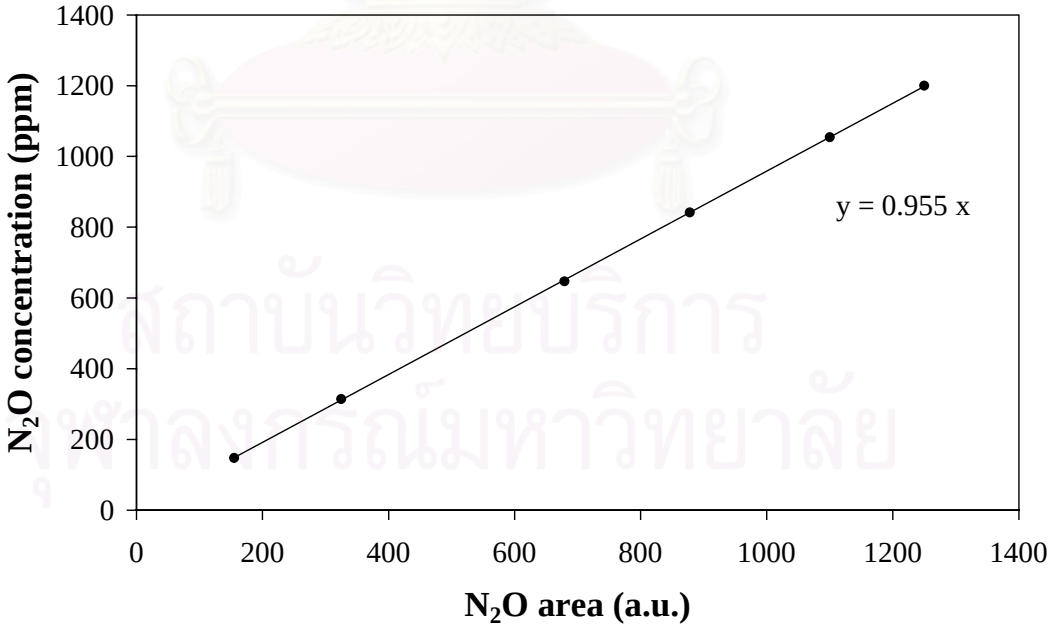

Figure B.7 The calibration curve of nitrous oxide

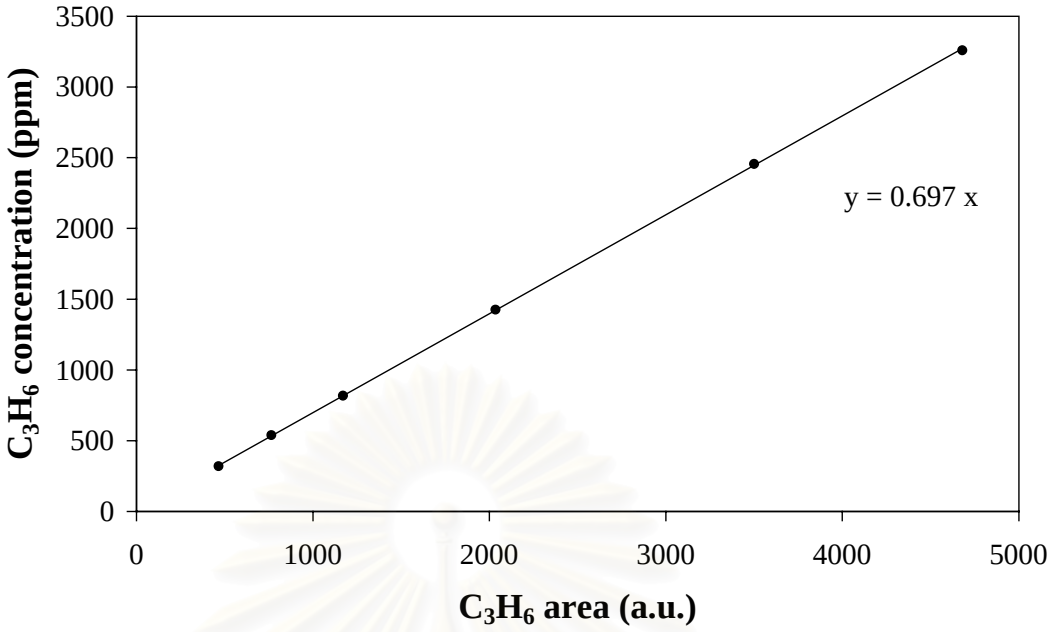

Figure B.8 The calibration curve of propene

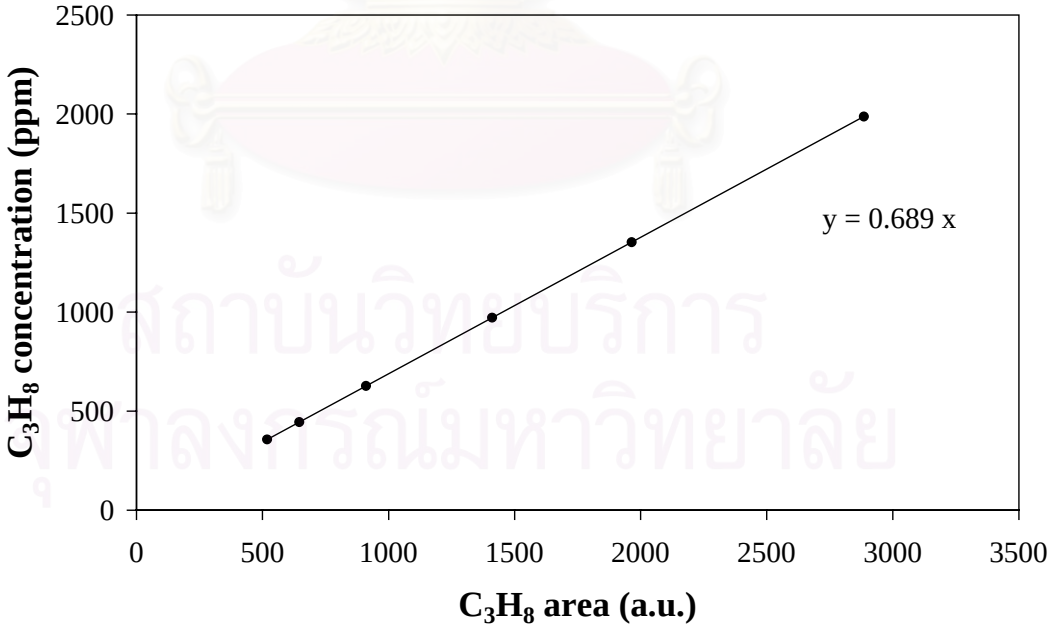

Figure B.9 The calibration curve of propane

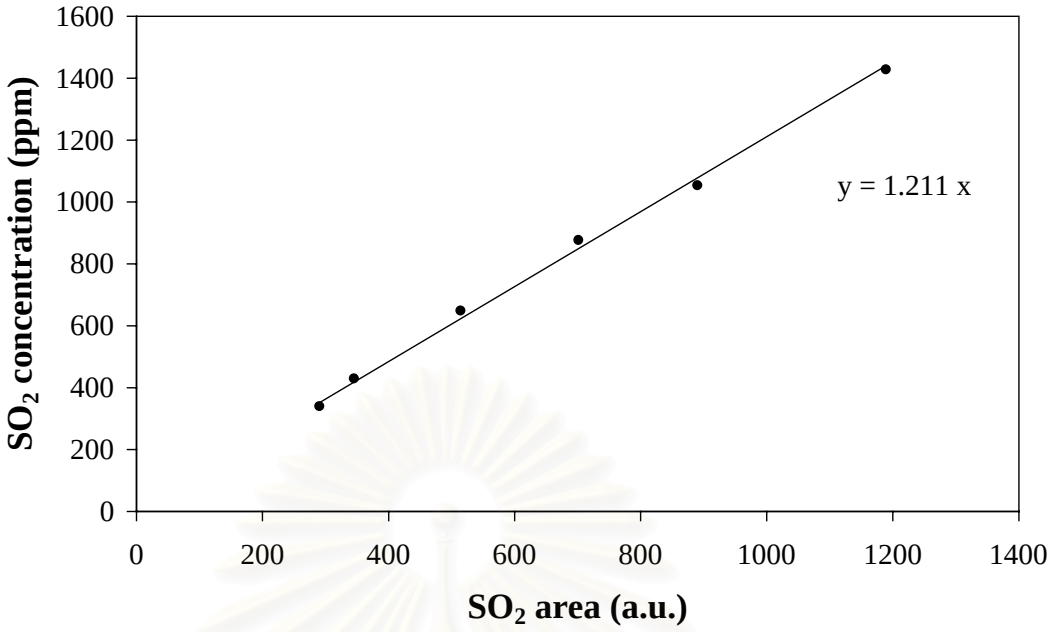

Figure B.10 The calibration curve of sulfur dioxide

APPENDIC C

CALCULATION OF CATALYST PREPARATION

The example of calculation shown is for 2wt% Ag/Al_2O_3 catalyst. The alumina support weight used for all preparation was 2.0 g.

Based on catalyst 100 g, in order to prepare 2wt% Ag/Al_2O_3, the catalyst is composed of

Silver	2	g.
Alumina support	98	g.

The silver compound used is silver nitrate ($AgNO_3$), which has a molecular weight 169.87 g, and the molecular weight of silver is 107.87 g.

The cluculation of the amount of each ingredient for required composition of the 2%wt Ag/Al_2O_3 catalyst is shown as follows:

For 2.0 g. of alumina support used:

- Silver amount

In 100 g of 2% Ag/Al_2O_3 catalyst has silver	=	2	g
In 100 g of 2% Ag/Al_2O_3 catalyst has alumina	=	98	g
If used support 2 g required silver	=	0.0408	g
Silver Nitrate ($AgNO_3$) 169.87 g has Silver	=	107.87	g
Silver 0.0408 g requires Silver Nitrate	=	0.3499	g
If used Ag/Al_2O_3 2 % requires Silver Nitrate	=	0.3499	g

APPENDIC D

CALCULATION OF SILVER METAL ACTIVE SITE ON CATALYST

The weight of catalyst used	=	w	g.
Area of N_2O peak afte adsorption	=	A	unit.
Average area of 50 μl. standard N_2O peak	=	B	unit.
Amounts of N_2O asorbed on catalyst	=	$\sum$(B-A)	unit.
Volume of N_2O adsorbed on catalyst	=	$[\sum(B-A)/B] \times 50$	μl.
Volume of gas 1 mole at 30°C	=	24.86×10^6	μl.
Mole of N_2O asorbed on catalyst	=	$[[\sum(B-A)/B] \times [50/24.86 \times 10^6]]$	

1 mole is 6.02×10^{23} molecule

Then, molecule of N_2O adsorbed on catalyst

$$= 2.01 \times 10^{-6} \times [\sum(B-A)/B] \times 6.02 \times 10^{23}$$

1 molecule of N_2O reacts with 2 molecule of silver metal as the equation

$$N_2O + 2Ag^o \rightarrow N_2 + Ag\text{-}O\text{-}Ag$$

Metal active site = $1.21 \times 10^{18} \times [\sum(B-A)/B]/w$ molecule of Ag^o/g.cat.

VITAE

Mr. Natthayak Kiattisirikul was born on 8th October, 1980, in Ayutthaya province, Thailand. He received her Bachelor degree of Science with a major in Chemical Engineering from Chulalongkorn University in March 1996. Since June 1, 1999, he has been studying for his master degree of Engineering from the department of Chemical Engineering, Chulalongkorn University.