

กลไกการกำจัดอินเทอร์มีเดียทของปฏิกิริยารีดักชันแบบเลือกเกิดของไนโตรเจนมอนอกไซด์ด้วย
โพรพิลีนโดยใช้ตัวเร่งปฏิกิริยาขณะที่มีก๊าซออกซิเจนอยู่มากเกินพอบนตัวเร่งปฏิกิริยาเอ็มเอฟไอ
แบบมีการแลกเปลี่ยนไอออนโคบอลต์



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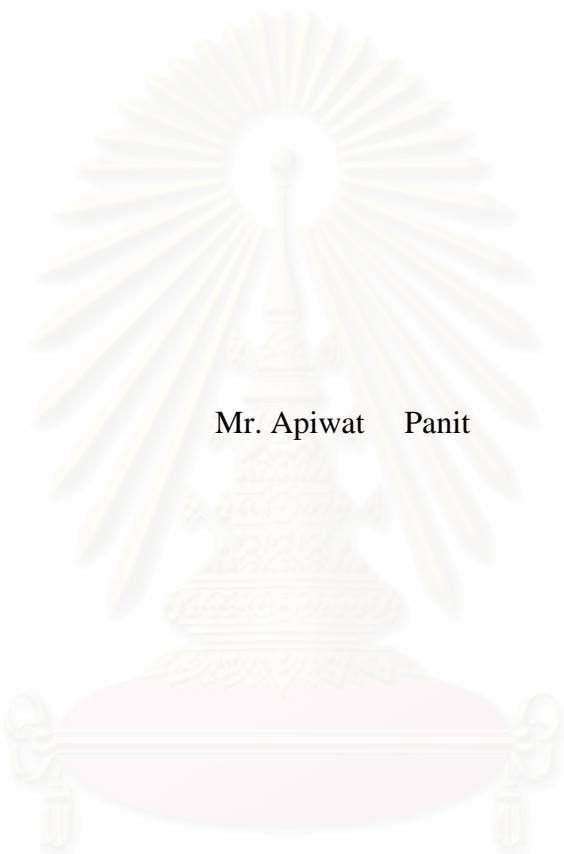
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REMOVAL MECHANISM OF INTERMEDIATES IN SELECTIVE CATALYTIC
REDUCTION OF NITROGEN MONOXIDE WITH PROPYLENE IN THE
PRESENCE OF EXCESS OXYGEN OVER
COBALT ION-EXCHANGED MFI CATALYST



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จุฬาลงกรณ์มหาวิทยาลัย
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อภิวัฒน์ พานิช : กลไกการกำจัดอินเทอร์มีเดียทของปฏิกิริยารีดักชันแบบเลือกเกิดของไนโตรเจนมอนอกไซด์ด้วยโพรพิลีนโดยใช้ตัวเร่งปฏิกิริยาขณะที่มีก๊าซออกซิเจนอยู่มากเกินพอบนตัวเร่งปฏิกิริยาเอ็มเอฟไอแบบมีการแลกเปลี่ยนไอออนโคบอลต์ (REMOVAL MECHANISM OF INTERMEDIATES IN SELECTIVE CATALYTIC REDUCTION OF NITROGEN MONOXIDE WITH PROPYLENE IN THE PRESENCE OF EXCESS OXYGEN OVER COBALT ION-EXCHANGED MFI CATALYST)

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งานวิจัยนี้ได้ศึกษากลไกการกำจัดอินเทอร์มีเดียทของปฏิกิริยารีดักชันแบบเลือกเกิดของไนโตรเจนมอนอกไซด์ด้วยโพรพิลีนโดยใช้ตัวเร่งปฏิกิริยาขณะที่มีก๊าซออกซิเจนอยู่มากเกินพบบนตัวเร่งปฏิกิริยาเอ็มเอฟไอแบบมีการแลกเปลี่ยนไอออนโคบอลต์โดยทำการทดลอง adsorption, desorption และ temperature program oxidation ทำการทดลอง adsorption เพื่อทดสอบกลไกการเกิดอินเทอร์มีเดียทสำหรับก๊าซผสมต่างๆ ทำการทดลอง desorption เพื่อไล่ก๊าซที่ไม่ได้ทำปฏิกิริยาไปเป็นอินเทอร์มีเดียทออกจากพื้นผิวของตัวเร่งปฏิกิริยา Co-ZSM-5 ส่วนการทดลอง temperature program oxidation นั้นทำเพื่อทดสอบกลไกการกำจัดอินเทอร์มีเดียทที่เกาะอยู่บนตัวเร่งปฏิกิริยา ผลการทดลองสามารถสรุปได้ว่าอินเทอร์มีเดียทที่เกาะบน Co-ZSM-5 นั้นเป็นปัจจัยสำคัญในการเกิดปฏิกิริยารีดักชันแบบเลือกเกิดของไนโตรเจนมอนอกไซด์ด้วยโพรพิลีนโดยใช้ตัวเร่งปฏิกิริยาขณะที่มีก๊าซออกซิเจนอยู่มากเกินพอ

สถาบันวิทยบริการ
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Removal mechanism of intermediates in selective catalytic reduction of nitrogenmonoxide with propylene in the presence of excess oxygen over cobalt ion-exchange MFI catalyst was investigated by using adsorption, desorption and temperature program oxidation (TPO) experiments. The adsorption experiment was conducted to test the mechanism of intermediate forming in different gas mixtures. The desorption experiment was conducted to purge the species that were not react to form intermediates deposit on Co-ZSM-5. The TPO experiment was conducted to test the mechanism of removing intermediates depositing on the catalyst. The results indicate that the intermediates depositing on Co-ZSM-5 catalyst play the important rules in selective catalytic reduction of NO with hydrocarbon over Co-ZSM-5 catalyst.

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CONTENTS

	PAGE
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGMENT.....	vi
LIST OF TABLE.....	ix
LIST OF FIGURE.....	x
CHAPTER	
I. INTRODUCTION.....	1
II. LITERATURE REVIEWS.....	4
III. THEORY.....	16
3.1 Origins and Effects of Nitrogen Oxides.....	16
3.1.1 Origins of Nitrogen Oxides.....	16
3.1.2 Effects of Nitrogen Oxides.....	16
3.2 Zeolites.....	18
3.2.1 Structure of Zeolites.....	18
3.2.2 Acidity of Zeolites.....	21
3.2.3 Ion-exchange Reaction in Zeolites.....	25
IV. EXPERIMENTS.....	26
4.1 Catalyst Preparation.....	26
4.2 Nitric Oxide Reduction.....	26
4.2.1 Chemicals and Reagents.....	26
4.2.2 Instruments and Apparatus.....	26
4.2.3 Procedure.....	28
4.3 Adsorption, Temperature Program Desorption and Temperature Program Oxidation Experiments.....	29
4.3.1 Adsorption Experiments.....	29
4.3.2 Temperature Program Desorption (TPD).....	29
4.3.3 Temperature Program Oxidation (TPO).....	29
4.4 Time-On-Stream Experiment.....	30
V. RESULTS AND DISCUSSIONS.....	31
5.1 Time-On-Stream (TOS).....	31
5.2 Effect of Hydrocarbon Species on Selective Catalytic	

Reduction of NO with Hydrocarbon.....	33
5.3 Study of Intermediates Formation by Variation of Adsorbed Gas Mixtures.....	38
5.4 Study of Intermediates Removal by Varying Oxidizing Gas Mixtures.....	41
5.5 The Influence of Time on Deposits.....	43
5.6 The Influence of Temperature on Deposits.....	43
5.7 Mechanism of the selective catalytic reduction of NO with propylene over Co-ZSM-5.....	47
VI. CONCLUSIONS AND RECOMMENDATIONS.....	52
REFERENCES.....	54
APPENDIX	58
VITA.....	61



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

TABLE	PAGE
4.1 Operating condition of gas chromatograph.....	28
5.1 Ratio of NO used for oxidized deposits per oxidized carbon from deposits calculated from TPO results after adsorbed by hydrocarbon and desorption.....	51



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

FIGURE	PAGE
3.1 Chemical transformations of atmospheric NO _x	17
3.2 Structure of type-Y (or X) zeolite.....	19
3.3 Structure of type-A zeolite.....	19
3.4 Skeletal diagram of the (001) face of mordenite.....	20
3.5 Structure of ZSM-5.....	20
3.6 Diagram of the surface of zeolite framework.....	23
3.7 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity.....	24
3.8 Lewis acid site developed by dehydroxylation of Bronsted acid site.....	24
5.1 N ₂ product concentration from reactor outlet as a function of time on stream of Co-ZSM-5 at temperature 550°C→400°C→550°C.....	32
5.2 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment on Co-ZSM-5 at 100°C.....	34
5.3 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment on Cu-ZSM-5 at 100°C.....	34
5.4 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment on H-ZSM-5 at 100°C.....	35
5.5 NO conversion as a function of temperature and hydrocarbon on Co-ZSM-5.....	35
5.6 NO conversion as a function of temperature and hydrocarbon on Cu-ZSM-5.....	36
5.7 NO conversion as a function of temperature and hydrocarbon on H-ZSM-5.....	36
5.8 CO ₂ concentration from reactor outlet of temperature programmed oxidation by O ₂ experiment on Co- and Cu-ZSM-5 after adsorption of propylene = 2000 ppm in He balance 100 cc/min, 0.7 g catalyst.....	37
5.9 CO ₂ concentration from reactor outlet of temperature programmed oxidation by O ₂ experiment on Co-ZSM-5 after adsorption experiment by varying gas mixtures and desorption.....	40
5.10 N ₂ concentration from reactor outlet of temperature programmed oxidation	

by O ₂ experiment on Co-ZSM-5 after adsorption experiment by varying gas mixtures after adsorption by varying gas mixture and desorption of Co-ZSM-5.....	40
5.11 CO ₂ concentration from reactor outlet of temperature programmed oxidation by varying oxidizing gas mixtures on Co-ZSM-5 after adsorption by [NO] = 1000 ppm, [C ₃ H ₆] = 2000 ppm, [O ₂] = 10%, 0.2 g Co-ZSM-5, GSHV ≈ 20000h ⁻¹	42
5.12 N ₂ concentration from reactor outlet of temperature programmed oxidation by varying oxidizing gas mixtures on Co-ZSM-5 after adsorption by [NO] = 1000 ppm, [C ₃ H ₆] = 2000 ppm, [O ₂] = 10%, 0.2 g Co-ZSM-5, GSHV ≈ 20000h ⁻¹	42
5.13 Amount of carbon on catalyst (mole) as a function of adsorbed time (minute).....	44
5.14 Amount of nitrogen on catalyst (mole) as a function of adsorbed time (minute).....	44
5.15 N/C ratio as a function of adsorbed time (minute).....	45
5.16 Amount of carbon on catalyst as a function of adsorbed temperature (C).....	45
5.17 Amount of nitrogen on catalyst as a function of adsorbed temperature (C).....	46
5.18 N/C ratio as a function of adsorbed temperature.....	46

CHAPTER I

INTRODUCTION

Nitrogen oxides (NO_x) are emitted primarily from transportation and industrial sources and contribute largely to a variety of environmental problem such as the formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone (smog), and general atmospheric visibility degradation. For these reasons, NO_x emissions are controlled. There are two major catalytic technologies for the abatement of the emission of nitrogen oxides into the atmosphere. One is the selective catalytic reduction using ammonia as a reductant (NH_3 -SCR). This is mainly use for stationary sources such as power plants. But there are problems about the use of ammonia such as ammonia slip, equipment corrosion, danger in transportation and storage of ammonia. The second technology is the three-way catalyst (TWC) that is efficient in the simultaneous reduction of CO, HC, and NO_x . However, it requires an exhaust gas composition operating very close to the stoichiometric point. The emissions from diesel and gas engines are not satisfactorily controlled. Because these emissions are both from small or mobile sources and contain excess oxygen, neither of the above two catalytic technologies is applicable. The same problem exists for such fuel-efficient engines as lean-burn gasoline engines. [1-4]

The most attractive method for the removal of NO_x is the catalytic decomposition of NO [5-7], because no reducing agent is required. Because NO is thermodynamically unstable relative to N_2 and O_2 [8]. This method is feasible. However, no suitable catalyst with a significant activity in real exhaust gas has been identified. It is widely accepted that the poisoning of the catalyst surface by oxygen from the exhaust gas or from the decomposition itself is the main problem. Therefore, up to now the only way to reduce NO_x emission in lean exhaust gas is the injection of reducing agents into the exhaust gas stream [9-13].

In 1986, Cu-ZSM-5 was reported to be much more active than the earlier known catalysts for the catalytic decomposition of NO. This finding was remarkable, but the catalytic activity decreased sharply with a decrease in the NO concentration and the catalyst suffered from severe deactivation in the presence of oxygen or sulfur oxides. It was later demonstrated that Cu-ZSM-5 showed a significant activity when it was used for a real lean-burn engine and, moreover, the rate increased in the presence of oxygen. It was shown that the reaction-taking place in this case was not the

decomposition of NO but the reduction of NO by hydrocarbons contained in the emission gas. Since then (1990-1992), many catalysts such as various kinds of solid acids and bases, including ZSM-5 loaded with metal ions (even with proton), were demonstrated to be active catalysts for this reaction. This reaction is called HC-SCR (selective catalytic reduction by hydrocarbons) [3].

The large worldwide reserves of natural gas and the availability of methane at gas-fired power plants make methane an attractive reductant for many applications. However, Cu-ZSM-5 and the acidic oxides that have been found to catalyze the selective catalytic reduction of NO_x with higher hydrocarbons are non-selective when methane is used as a reducing agent. Only a few catalysts have been reported to selectively catalyze the reduction of NO_x, rather than the complete combustion of methane, in an oxidizing atmosphere [13].

Li and Armor were the first to report that NO could be selectively reduced by methane in the presence of excess oxygen over a cobalt ion-exchanged ZSM-5 zeolite (Co-ZSM-5). This reaction could find an application as a NO_x control method in lean-burn natural gas fueled vehicles. The catalytic activity of Co-ZSM-5 was found to be low in the absence of oxygen and was significantly enhanced in the presence of excess oxygen. The NO conversion increased with the methane level, although a relatively small amount of methane was needed for complete NO reduction because of the high selectivity of methane towards the NO reduction reaction. Additional screening tests revealed that Ni- and Mn-exchanged ZSM-5 zeolites were also active for this reaction, Fe-, Cu-, and H-ZSM-5 zeolites exhibited very low activities, while Cr- and the parent Na-ZSM-5 were completely inactive. These results suggested that the nature of the transition metal cation is crucial. Li and Armor studied the effect of the zeolite structure. Using methane as the reducing agent, the authors compared a number of cobalt exchanged zeolites and found Co-ZSM-5 to be the most active one [14,15].

Due to Co-ZSM-5 is an attractive catalyst because of its high activity in SCR of NO with methane comparing to other ion-exchanged ZSM-5, there were many literatures that studied the SCR of NO with methane over Co-ZSM-5. But there were less literatures that concerned the SCR of NO with other hydrocarbon especially propylene, then it was interesting to investigate this SCR reaction with other hydrocarbon such as propylene. On the other hand, from many literatures that mention the mechanisms of this reaction [4, 22, 32, 33, 35, 36, 37, 39, 46], the proposed

mechanisms of SCR of NO with hydrocarbon over Co-ZSM-5 of various hydrocarbons (methane, propane, propylene) were the similar scheme that contained two main steps, intermediates forming and intermediates removing. Since the intermediates formation reaction were depended on type of loaded cation on ZSM-5 zeolites and type of hydrocarbon. For example, if methane was used, there would be nitromethane (CH_3NO or CH_3NO_2) presented as intermediates depositing on catalyst surface. But the intermediates of methane deposit weakly on Co-ZSM-5, thus, it can be oxidized easily forming products and the deposits accumulation would not be occur. In this case, if methane was used for this work, there would not appropriate because this work was the observation of the phenomenon of deposits formation and removal mechanism that the intermediates of methane could not be supported. Since, there were the similar scheme of mechanism of these reactions of various hydrocarbons but there were different only the type of intermediates. Hence, to investigate the reaction mechanism by the adsorption technique the hydrocarbon that was chosen must active to form deposits accumulation, thus, in this case, methane was not an appropriate choice, then propylene was chosen because of was very active to form deposits accumulation in the SCR reaction on catalyst surface. So, in this study, the mechanism of SCR of NO with propylene in the presence of excess oxygen over Co-ZSM-5 was investigated using sets of experiment such adsorption, desorption and temperature programmed oxidation experiment.

1.1) Thesis objectives

To study the removal mechanism of intermediates in selective catalytic reduction of NO with propylene in the presence of excess oxygen on Co-ZSM-5 catalyst.

1.2) The scope of this study

- 1.2.1) Study the effect of hydrocarbons (C_3H_6 and C_3H_8) on the SCR reaction activity over Co-ZSM-5.
- 1.2.2) Study the catalytic mechanism of the prepared catalysts for the selective catalytic reduction of NO with propylene in the presence of excess oxygen by adsorption, desorption and temperature program oxidation experiments.
- 1.2.3) Study the effect of deposits on SCR reaction activity by time on stream experiment.

CHAPTER II

LITERATURE REVIEWS

Selective catalytic reduction of nitric oxide with hydrocarbon was a technology that has been interested and developed since it was discovered. Because it can remove nitric oxides even in the presence of excess oxygen, whereas present automotive catalysts can not work effectively under this condition. This chapter present about the studies of this kind of technology and related subjects that had been studied by many researchers as follows.

The catalytic decomposition of nitrous oxide to nitrogen and oxygen was studied over a number of catalysts by Li and Armor (1992) [17]. Copper and cobalt exchanged ZSM-5, mordenite, zeolite beta, ZSM-11 and ferrierite are much more active than other cation exchanged zeolites (Cu/Y, Co/Y, Co-ferrierite, Cu/L, Co/L, Ni/ZSM-5, Mn/ZSM-5) and metal oxide (CuO/Al₂O₃, and CoO/Al₂O₃). For noble metal catalysts, a cation exchanged ZSM-5 has higher activity than the Al₂O₃ supported form. Rhodium is the most active catalyst, but surprisingly Pt/ZSM-5 is one of the least active catalysts of all. They also evaluated the effects of oxygen and nitric oxide addition, metal loading and pretreatment upon the catalyst activity too.

US. Patent No. 5-149-512 (1992) [16] issued to Li and Armor describes the invention of a catalytic process for destroying NO_x from oxygen-containing combustion products wherein methane serves as a reductant. The process comprises contacting the NO_x-containing combustion products with a desired amount of methane and oxygen in the presence of a metal-exchanged crystalline zeolite having a silicon to aluminum ratio of greater than or equal to about 2.5 under conditions sufficient to effect conversion to gaseous nitrogen, water and carbon oxides. The zeolites are exchanged with a cation selection from the group consisting of cobalt, nickel, iron, chromium, rhodium and manganese.

Li and Armor (1992) [14] reported the discovery of a family of catalysts that can effectively reduce NO_x with methane in the presence of excess oxygen. This new catalytic chemistry offers an alternative means for controlling NO_x emission. Complete reduction of nitric oxide was obtained at 400°C over a Co/ZSM-5 catalyst.

The presence of oxygen in the feed greatly enhances the nitric oxide reduction activity on Co/ZSM-5, and the nitric oxide conversion is strongly related to the inlet methane level. On the other hand, Cu/ZSM-5, which is a unique catalyst for the direct nitric oxide decomposition, is a poor catalyst for nitric oxide reduction by methane in the presence of excess of oxygen.

Li and Armor (1993) [15] further investigated the catalytic reduction of NO_x with methane in an oxidizing atmosphere over many kinds of metal exchanged zeolites, e.g., ZSM-5 and mordenite, are active catalysts for reduction. For Co/ZSM-5 catalyst, the nitric oxide conversion displays a volcano-shape curve as temperature increases, which is reversible upon decreasing temperature. The nitric oxide reduction activity is proportional to the level of Co^{2+} exchanged into ZSM-5, but excess amounts of cobalt do not contribute to the activity. Mn/ZSM-5 is very similar to Co/ZSM-5 in the nitric oxide reduction activity, and Ni/ZSM-5 has slightly lower activity compared to Co/ZSM-5. Under an oxidizing condition, Cu/ZSM-5, however, is ineffective for the nitric oxide reduction. Co/Y, which has much more Co^{2+} , is much less active compare to Co/ZSM-5, or Co-mordenite. The amount of nitric oxide adsorbed, measured by temperature programmed desorption (TPD), on Co/Y is extremely small NO/Co (0.6) compare to Co/ZSM-5 (>1.1) and Co- mordenite (0.8).

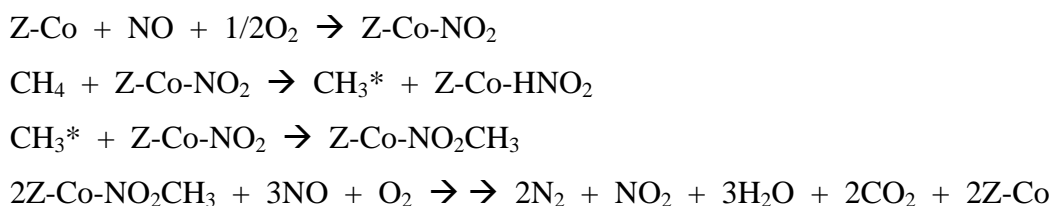
Armor et al. (1993) [18] investigated the effect of water vapor on the selective reduction of NO with CH_4 in excess O_2 over a Co/ZSM-5 catalyst. The presence of 2% water significantly decreases the NO conversion at $T \leq 450^\circ\text{C}$ but has less of an effect at $T \geq 500^\circ\text{C}$. The selectivity of methane toward NO reduction was enhanced by the presence of water at low temperatures and is unchanged at high temperatures. This inhibition is reversible upon eliminating water from the system. The effect of water is dependent on the level of water added, space velocity, reaction temperature, and level of methane in the feed. The addition of water increases the empirical reaction order with respect to either CH_4 or NO from a fractional order to first order. Temperature-programmed desorption studies show that the amount of NO adsorption on Co/ZSM-5 is significantly reduced if it is not fully dried, and the competitive adsorption between H_2O and NO is probably the cause of the inhibition by water. In

addition, Co/ZSM-5 is capable of removing NO and CO simultaneously in either a dry or wet feed.

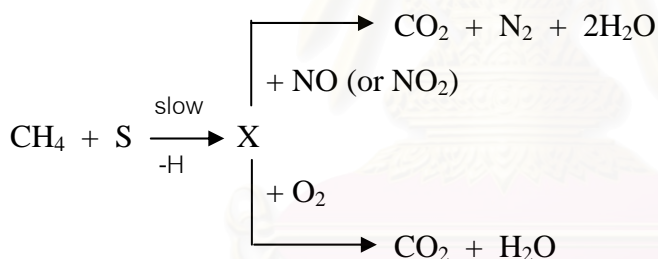
Ansell et al. (1993) [44] studied mechanism of the lean NO reaction over Cu/ZSM-5 by used transient techniques. The activation of propene and nitric oxide by Cu/ZSM-5, in the presence and absence of oxygen, have been investigated by TAP to elucidate the nature of the reducing species involved in the formation of nitrogen. Propene was converted to long-lived (carbon-rich) species on the zeolite whether oxygen was present or not, and it was these deposited species which acted as a reductant in this catalytic system. The ability of coke to reduce nitric oxide was significantly enhanced by the presence of oxygen. The crucial role of the oxygen appeared to be to induce the generation of an adsorbstate of NO_x on the exchanged-Cu sites; these NO_2 -type species existed at temperature characteristic of high lean NO_x activity. During temperature programmed reaction under a fuel-lean (oxidizing) exhaust gas, both nitric oxide and propene were retained at lower temperature; as the temperature rose, so propene retention (as coke) and total oxidation begin to complete. However, there were sufficient reducing species still present on the surface to allow substantial reduction of the $-\text{NO}_2$ species, as the latter approach their limit of thermal stability.

Ditri et al. (1993) [45] studied the role of oxygen in the selective reduction of nitrogen monoxide by either propane or propene over "excessively" ion-exchanged Cu/ZSM-5. In a wide temperature region and in the absence of additives such as steam, propane is a more effective reductant than propene; with propane and in the presence of oxygen reduction of nitric oxide to nitrogen approaches 100% above 600 K. The difference in effectiveness is due to the different degree of catalyst deactivation by carbonaceous deposits: more carbonaceous material is deposited from propene than from propane. Temperature-programmed oxidation shows that above 600 K the rate of oxidation of carbonaceous deposits by oxygen is significant. The amount of such carbonaceous deposits is, therefore, lower when catalytic tests above 600 K are done in the presence of oxygen. At very high temperatures, the in situ volatilization of the deposits by reaction with oxygen keeps the catalyst surface clean in the steady state of nitric oxide reduction.

Li et al. (1994) [33] proposed a mechanism for NO-CH₄-O₂ over Co-ferrierite as described below, in which CH₄ is activated by NO₂ adsorbed on Co ion.



Cowan et al. (1995) [36] determined the relative reaction rates of CH₄ and CD₄ with NO in the presence of excess oxygen over a Co-ZSM-5 catalyst. One interpretation consistent with the results is that the rate-determining step involves detachment of hydrogen from methane by adsorbed nitrogen dioxide to form a methyl species which reacts further with a nitrogen oxide in one pathway by with oxygen in the other. The scheme as follows is suggested in which a surface species S abstract hydrogen to form an intermediate X which reacted further in two different ways.



Li and Armor (1995) [19] evaluated the effect of SO₂ on catalytic performance for the reaction of selective reduction of NO by CH₄ in the presence of O₂ over Co/ZSM-5 and Co-ferrierite with and without the presence of water vapor. Over a Co/ZSM-5 catalyst, in the absence of added H₂O the addition of 53 ppm SO₂ slightly decreased the NO conversion at 500°C but doubled the NO conversion at 550 and 600°C. With the coexistence of 53 ppm SO₂ and 2% H₂O, a substantial decrease in NO conversion was found at T ≤ 550°C but no effect was observed at 600°C. Over a Co-ferrierite catalyst, the addition of 53 ppm SO₂ caused a sharp decrease in NO conversion. With both catalysts, CH₄ conversion was significantly reduced and the CH₄ selectivity greatly enhanced as the result of SO₂ addition. Temperature-programmed desorption measurement of NO adsorbed on fresh and SO₂ exposed

catalysts revealed that ca. 26% of Co^{2+} sites were covered by SO_2 in both Co/ZSM-5 and Co-ferrierite catalysts during a steady-state reaction at 550°C . In addition, the degree of impact of SO_2 on catalyst performance provides further insight about the catalyst sites.

Cant et al. (1995) [20] determined the rate-determining step in the selective reduction of nitric oxide by methane over a Co/ZSM-5 catalyst in the presence of oxygen. They studied the relative reaction rate of CH_4 and CD_4 with NO in excess oxygen condition. The rate ratio, CH_4 consumption versus CD_4 consumption, is nearly 2.4 when using a dry feed at 375°C . Experiments at 431°C using a feed containing 1.6% H_2O show a rate ratio of 2.05. These values are close to those expected for a primary kinetic isotope effect at the respective temperature, and it is therefore concluded that the rate-determining step is the breaking of a carbon hydrogen bond. The kinetic isotope effect is slightly less for the selective reaction with NO than for the concurrent direct oxidation of methane by oxygen. The two reactions have very similar kinetic orders in methane, suggesting that a common intermediate is involved in the two pathways. Hydrogen-deuterium exchange between CD_4 and H_2O to make CH_3D is negligible under conditions. Similarly, mixed feeds of CH_4 and CD_4 show very little exchange. One interpretation consistent with the results is that the rate-determining step involves detachment of hydrogen from methane by adsorbed nitrogen dioxide to form a methyl species, which reacts further with a nitrogen oxide in one pathway but with oxygen in the other.

Lukyanov et al. (1995) [34] studied the selective catalytic reduction (SCR) of NO with methane over Co/ZSM-5 and H-ZSM-5 zeolites. The conclusions as follow.

- (i) The SCR reaction involves free radical chemistry and may be partly homogeneous.
- (ii) These reaction are initiated on the catalyst surface. Combustion may be initiated in the homogeneous gas phase at somewhat higher temperatures.
- (iii) NO_2 appears to be involved in initiating radical formation; an important function of O_2 may be to convert NO into NO_2 .

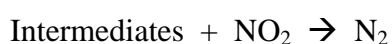
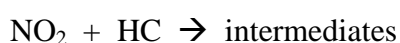
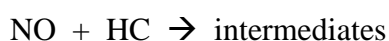
(iv) N_2 formation requires a catalyst; combustion does not, suggesting that an intermediate is formed on the catalyst surface which can couple with NO or NO_2 to form the N-N bond.

(v) In the absence of a catalyst, combustion is not initiated by either NO or O_2 alone up to 873 K, but light-off occurs below 773 K when both are present, and at still lower temperatures with NO_2 . This homogeneous combustion imposes an upper limit on the temperature for the SCR of NO_x by hydrocarbons in the presence of excess O_2 .

Guyon et al. (1996) [46] used Two-step experiments to investigate the mechanism of NO_x reduction with propylene over copper ion-exchanged ZSM-5 zeolites. The first step was the formation of a reactive intermediate and the second one the reaction of this intermediate during a transient regime without any hydrocarbon injection. The presence of NO or NO_2 appears to be mandatory to obtain such an intermediate. In contrast, the presence of oxygen is not necessary, The intermediate reacts only with NO_2 as well as with O_2 . The role of oxygen could be to oxidize NO to NO_2 in a first reaction step. There main conclusions can be summarized as follows:

- A reactive intermediate is only generated over the catalyst from NO or NO_2 and propene. The injection of O_2 is not mandatory.
- This intermediate only reacts with NO_2 , not with NO, to give nitrogen.
- Oxygen allows the oxidation of NO to NO_2 and completes with NO_2 to react with the intermediate.

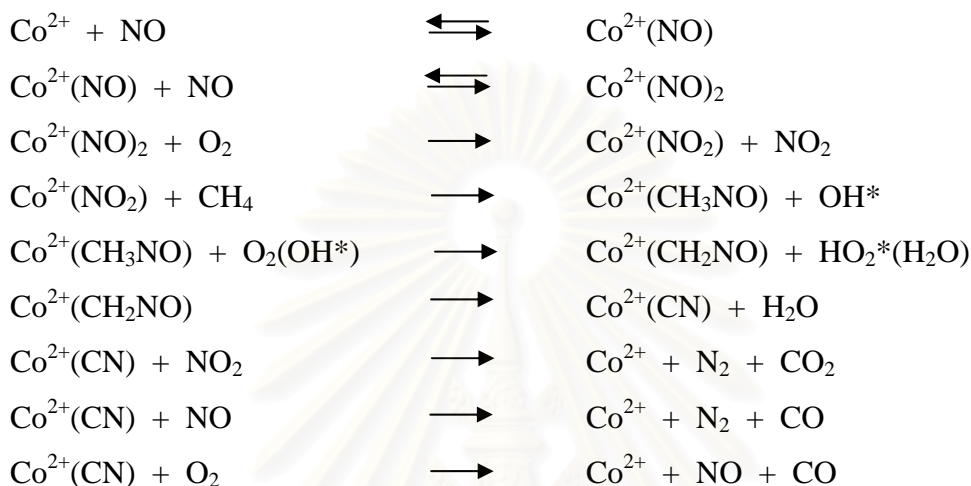
An overall mechanism for NO reduction over Cu-ZSM-5 zeolite can be proposed as follow.



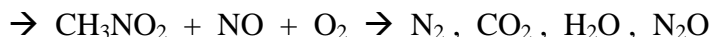
Lukyanov and coworkers (1996) [21] studied the selective catalytic reduction (SCR) of NO with methane over Co/ZSM-5 and H-ZSM-5 zeolites by investigation the role of free radicals and competitive oxidation reactions in the reaction of CH₄ with NO, NO₂, and O₂, and with the mixtures of NO_x+O₂. Based on the comparison of the “light-off” temperature as well as the activation energies of these reaction, a conclusion is draw that over both catalysts at temperatures below 500°C NO reduction into N₂ and CH₄ oxidation into CO_x are coupled and initiated by the reaction of CH₄ with NO₂. The results demonstrate that this reaction may be considered as a limiting reaction step of NO₂ reduction into N₂, and of the SCR reaction for the mixture of CH₄+NO+O₂ when O₂ is present in large amounts. With the latter mixture when O₂ concentration is relatively low (up to about 1.5%) another reaction step, namely, the catalytic oxidation of NO by O₂ into NO₂ appears to control the rate of the SCR process. Thus, an important role of O₂ is to convert NO into NO₂. At low temperature (below 400°C) O₂ does not compete with NO_x for CH₄, but even at these temperatures O₂ participated in oxidation of the intermediate reaction species decreasing in this way the selectivity of the SCR process. At higher temperatures (above 450°C) a strong competition between O₂ and NO_x for CH₄ is observed and this results in a further decrease in the process selectivity. It is shown that the higher SCR selectivity of H-ZSM-5 catalyst in comparison with Co/ZSM-5 is due to the stronger competition between O₂ and NO₂ for CH₄ over the latter catalyst. The effects of space velocity and reactor size were briefly explored. These results show that the reaction pathways are the same for both catalysts studied in this work. Based on these, and literature results, the formation of CH₃• free radical and possible reaction of this radical with NO_x and O₂, that form the pathways of the SCR process, are postulated. Also, the possible role of gas phase reactions in the SCR process is considered.

Aylor et al. (1996) [37] conducted in situ infrared investigation of the reduction of NO by CH₄ over Co-ZSM-5. In the presence of O₂, NO₂ is formed via the oxidation of NO. Adsorbed NO₂, then reacts with CH₄. Nitrile species are observed and found to react very rapidly with NO₂, and at a somewhat slower rate with NO and O₂. The dynamics of the disappearance of CN species suggests that they are reactive intermediates, and that N₂ and CO₂ are produced by the reaction of CN species with NO₂. While isocyanate species are also observed, these species are

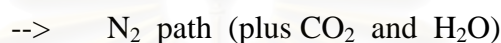
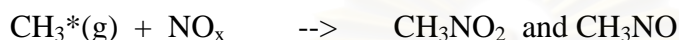
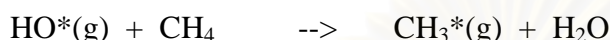
associated with Al atoms in the zeolite lattice and do not act as reaction intermediates. A mechanism for NO reduction is proposed that explains why O₂ facilitates the reduction of NO by CH₄, and why NO facilitates the oxidation of CH₄ by O₂. The proposed reaction mechanism for NO reduction by CH₄ in the presence of O₂ show below.



T. Sun et al. (1996) [22] studied NO reduction with methane over Co-ZSM-5 in an oxidizing atmosphere. Although the activity was reduced due to the poisoning of oxygen, NO decomposed over Co-ZSM-5 to nitrogen and oxygen in two different temperature ranges, 100-300°C and >400°C. This suggests the presence of two types of Co²⁺ cations in ZSM-5. The adsorption of NO, NO₂ and CH₄, as well as the reduction of NO with methane in O₂ were studied with in-situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFT). NO and methane molecules were only weakly adsorbed on Co-ZSM-5, and would desorb completely at the reaction temperature. The presence of oxygen was found to enhance the NO interaction with Co-ZSM-5, leading to the formation of adsorbed NO₂ intermediates. The adsorbed NO₂ would activate methane molecules and yield hydrogen and methyl radicals, which could in turn react with NO₂ to generate nitromethane intermediates. A tentative reaction mechanism has been proposed to elucidate the production of N₂, N₂O, H₂O, formaldehyde and CO₂. This literature also explained the reduction scheme with methane over Co-ZSM-5 by following scheme:



Lombardo et al. (1998) [35] studied the reactions of nitromethane with NO_2 or NO in the presence of excess O_2 . The proposed mechanism as follows:



From the literature of Misono (1998) [4], it mentioned the mechanism for NO reduction in the systems $\text{NO-C}_3\text{H}_6\text{-O}_2$ catalyzed by Ce-ZSM-5 . Relative reactivities in the order of $\text{NO}_2\text{-HC-O}_2 \approx \text{NO}_2\text{-HC} \gg \text{NO-HC-O}_2 > \text{NO-HC}$ is one of the experimental facts to support this mechanism. It proposed that selective catalytic reduction by propylene ($\text{C}_3\text{H}_6\text{-SCR}$) over Ce-ZSM-5 proceeds by the following three-step mechanism.



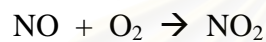
Where X is an organic nitro and/or nitrite compound. The importance of the first step is evident, for example, from the following fact. Na-ZSM-5 , which has little activity for the oxidation of NO to NO_2 , is not active for NO reduction in a mixture $\text{NO-C}_3\text{H}_6\text{-O}_2$, but becomes active when NO_2 is used instead of NO , in a $\text{NO}_2\text{-C}_3\text{H}_6\text{-O}_2$ reaction. This also indicates that Ce (or a proton) catalyzes the oxidation of NO . Once NO is oxidized to NO_2 the subsequent reactions with C_3H_6 are rather fast for both Na- and Ce-ZSM-5 catalysts. The reaction between C_3H_6 and NO_2 occurs even on the surface of silica at low temperature, as detected by IR. But the rate of N_2 formation is still slower for Na-ZSM-5 than for Ce-ZSM-5 , showing that the $\text{NO}_2\text{-C}_3\text{H}_6$ reaction to form N_2 is accelerated more by cerium than by sodium or by protons.

Goryashenko et al. (1998) [32] studied the mechanism of the selective catalytic reduction of NO with propylene over Co-ZSM-5 using in-situ FT-IR. Their proposed mechanism as follows:

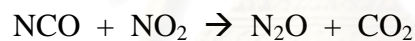
- Hydrocarbon is activated by NO or NO_x leading to the formation of surface NCO species.



- NO is oxidized to NO₂ by oxygen on isolated Co cation of the Co-ZSM-5 catalyst.



- NCO intermediates adsorbed on Al³⁺ and Co²⁺ cation interact preferentially with NO₂ formed on the Co cation leading to N₂, CO₂, and N₂O.



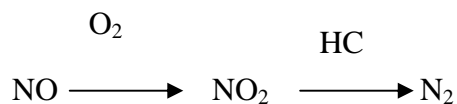
From literature of Misono [4], it mentions that, focusing on the initial step of the NO transformation, the mechanism proposed so far are divided into three major classes.

- 1.) It was first believed that NO reacts directly with partially oxidized hydrocarbons (HC-O) like aldehydes and alcohols:



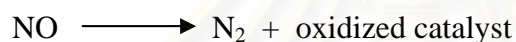
This mechanism is consistent with the fact that the reduction of NO starts at almost the same temperature with the oxidation of the hydrocarbons and that easily oxidizable alcohols and aldehydes are usually much more efficient reductants than hydrocarbons.

- 2.) In the second mechanism, NO is first oxidized to NO₂ which then (adsorbed or in the gas phase) reacts with HC.



Note that olefins readily react with NO_2 , whereas reaction with methane is slow. Hamada and coworkers proposed this mechanism for NO reduction over alumina and H-ZSM-5 catalysts, based principally on the higher reactivity of $\text{NO}_2\text{-HC-O}_2$ than NO-HC-O_2 , as well as on the positive effect of oxygen on the latter reaction. A similar mechanism has been proposed for $\text{NH}_3\text{-SCR}$.

3.) The third mechanism is the direct decomposition of NO which forms N_2 and oxidized surface of catalyst, the latter being reduced by HC. Pt catalysts possibly follow this mechanism.



The second mechanism, involving NO_2 as the intermediate, probably operates in most cases. But it must be remembered that the dominant mechanism varies depending on the catalyst, the reductant, and the reaction conditions.

From these three mechanisms mention by Misono [4] and the proposed mechanism from many literatures described above. There can be concluded that the mechanism of SCR of NO with hydrocarbon (whatever hydrocarbon, methane, propane or propylene) over Co-ZSM-5 was the same as the second mechanism that NO is first oxidized to NO_2 which then reacts with hydrocarbon forming intermediates and then the intermediates react forward producing nitrogen products.

Hence, the reaction mechanisms of selective catalytic reduction of NO with hydrocarbon over Co-ZSM-5 catalyst were proposed that it contain two main steps;

- (1) The hydrocarbon activation leading to the N-containing intermediates.
- (2) The N-containing intermediates convert to the final products.

In this thesis, the adsorption experiments were conducted to test the mechanism of forming intermediates, the temperature program desorption and

temperature program oxidation were conducted to test the mechanism of removing intermediates converting to the final products.



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CHAPTER III

THEORY

3.1) Origins and Effects of Nitrogen Oxides [1]

3.1.1) Origins of Nitrogen Oxides

The major source of nitrogen oxides is the combustion of fossil fuels such as coke in electrical power plants or petroleum in the engines of vehicles and airplanes. In both cases, the processes are so fast that the thermodynamic equilibrium ($\text{CO}_2 + \text{H}_2\text{O}$) is not reached. For this reason, the exhaust gases contain products of an incomplete combustion such as soot or carbon monoxide. Nitrogen oxides are also formed. Among them, nitrogen monoxide (NO) accounts for 95% of all nitrogen oxide emissions. From a thermodynamic point of view, this compound is unstable. The majority of NO is formed by the reaction between nitrogen and oxygen following the mechanism established by Zeldovich.



3.1.2) Effects of Nitrogen Oxides

In recent years, studies from within a variety of the biological sciences have converged to reveal the importance of NO to the living organism. One of these reports described NO as an essential messenger, which transmits the necessary information to the white corpuscles within the bloodstream to destroy cells and assorted bacteria and, in a second role, to the neurotransmitters to dilate the blood vessels. However, while the biologically active NO is a poisonous product of the in vivo enzyme-catalyzed transformation of the amino acid, arginine, and is maintained only at beneficent concentrations, that emitted freely from a car engine presents a real hazard of toxicity.

In the presence of air NO is oxidized to NO_2 , which is rapid conversion at high concentration, further accelerated in the presence of sunlight and hydrocarbon from

unburned gasoline. This oxide is poisonous for the respiratory system, provoking both lung infection and respiratory allergies since it is able to diffuse through the alveolar cells and capillary vessels of the lungs and damage their structure through their propensity towards oxidation. Epidemiological studies have revealed that concentrations of nitrogen oxides having hazardous effects for people in good health are above 0.05 ppm for an exposure of over 24 h. Nevertheless, this value is often exceeded in towns with dense traffic during peak hours or during the summer.

Nowadays, the deforestation of the hemisphere by contamination is considered one of the most important ecological problems. Although responsibility might be directed towards a variety of factors, that of acid rain remains a major contributor among them. In this process, nitrogen oxides play an influential role in the photochemistry of both stratosphere and stratosphere. The chemical transformations of nitrogen oxides are summarized in Fig. 3.1.

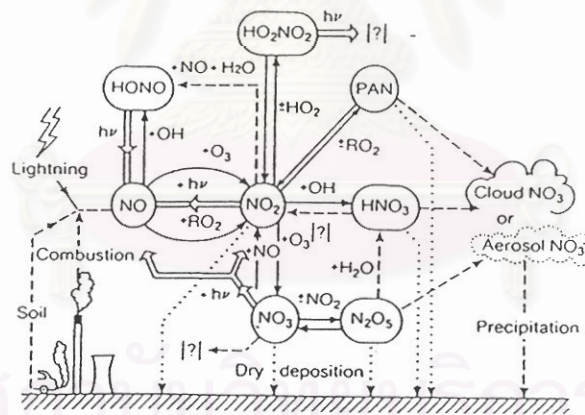


Fig. 3.1 Chemical transformations of atmospheric NO_x : (\Rightarrow) photochemical processes, (\rightarrow) thermal gas-phase processes, ($\bullet\bullet\bullet$) dry deposition, and (---) heterogeneous reactions [1].

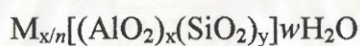
3.2) Zeolites

3.2.1) Structure of Zeolites [28]

Zeolites are crystalline aluminosilicates that develop uniform pore structure having minimum channel diameter of 0.3 to 1.0 nm. The size depends primarily upon the type of zeolite. Zeolites provide high activity and unusual selectivity in a variety of acid-catalyzed reactions. Most of the reactions are caused by the acidic nature of zeolites. This section will discuss the acidic properties of zeolites.

The structure of zeolites consists of a three-dimensional framework of SiO_4 or AlO_4 tetrahedra, each of which contains a silicon or aluminum atom in the center. The oxygen atoms are shared between adjoining tetrahedra, which can be present in various ratios and arranged in a variety of ways. The framework thus obtained contains pores, channels, and cages, or interconnected voids.

Zeolites may be represented by the general formula,



when the term in brackets is the crystallographic unit cell. The metal cation of valence n is present to produce electrical neutrality since for each aluminum tetrahedron in the lattice there is an overall charge of -1 .

The frameworks of zeolites used most frequently as adsorbent or catalyst are shown in Figs. 3.2-3.5. The Al or Si atoms are located at the intersection of lines that represent oxygen bridges. The X and Y zeolites are structurally and topologically related to the mineral faujasite and frequently refer to as faujasite-type zeolites. The two materials differ chemically by their Si/Al ratios, which are 1-1.5 and 1.5-3.0 for X and Y zeolite, respectively. In faujasites, large cavities of 1.3 nm in diameter (supercages) are connected to each other through apertures of 1.0 nm.

In type A zeolite (Fig. 3.3.), large cavities are connected through apertures of 0.5 nm, determined by eight-member rings.

The mordenite pore structure (Fig. 3.4) consists of elliptical and noninterconnected channels parallel to the c -axis of the orthorhombic structure. Their openings are limited by twelve-member rings (0.6-0.7). ZSM-5 zeolite (Fig. 3.5) shows a unique pore structure that consists of two intersecting channel systems: one

straight and the other sinusoidal and perpendicular to the former (Fig. 3.5). Both channel systems have ten-member-ring elliptical openings (5.5 Å in diameter).

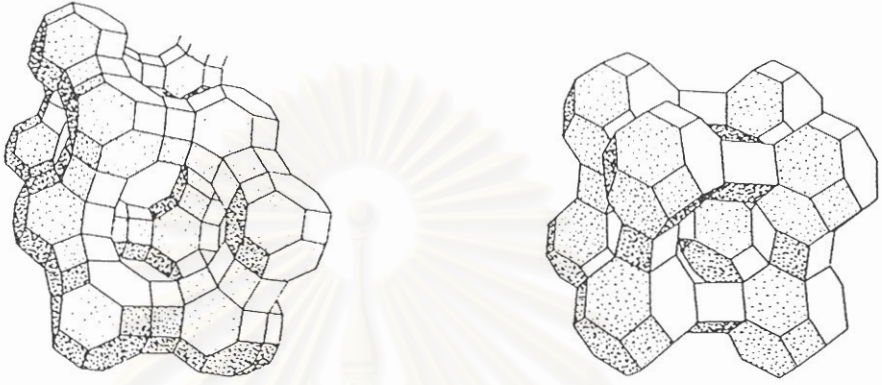


Fig. 3.2 Structure of type-Y (or X) zeolite [28] Fig. 3.3 Structure of type-A zeolite[28]

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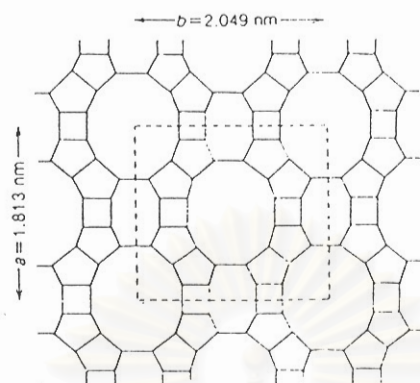


Fig. 3.4 Skeletal diagram of the (001) face of mordenite [28]

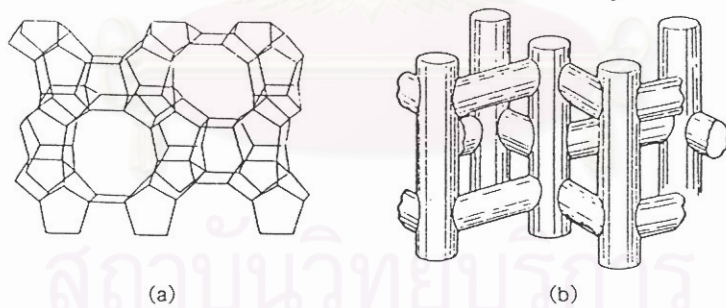


Fig. 3.5 Structure of ZSM-5 (a) Skeletal diagram of the (001) face of ZSM-5 (b) channel network [28]

3.2.2) Acidity of Zeolites

Classical Bronsted and Lewis acid models of acidity have used to classify the active sites on zeolites. Bronsted acidity is proton donor acidity; a trigonally coordinated alumina atom is an electron deficient and can accept an electron pair therefore behaves as a Lewis acid [23,24].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [25]. Since the number of acidic OH groups depend on the number of aluminum in zeolites framework, decrease in Al content is expected to reduce catalytic activity of zeolite.

Based on electrostatic consideration, the charge density at a cation site increase with increasing Si/Al ratio. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to the difference in the order of aluminum in zeolite crystal [24].

It has been reported the mean charge on the proton was shifted regularly towards higher values and the Al content decreased [23]. Simultaneously, the total number of acidic hydroxyls governed by the Al atoms, were decreased. This evidence emphasized that entire acid strength distribution (weak, medium, and strong) was shifted towards stronger values. That is, weaker acid sites become stronger with the decrease in Al content.

An improvement in thermal or hydrothermal stability has been ascribed to the lower density of hydroxyls groups which parallel to that of Al content [26]. A longer distance between hydroxyl groups decreases the probability of dehydroxylation that generates defects on structure of zeolites.

Protonic acid centers of zeolite are generated in various ways. Figure 3.6 depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [27].

Acidic OH groups can be produced also by ion-exchange with polyvalent cations such as Ca^{2+} , Mg^{2+} , or La^{3+} . The development of acidity can be expressed as:

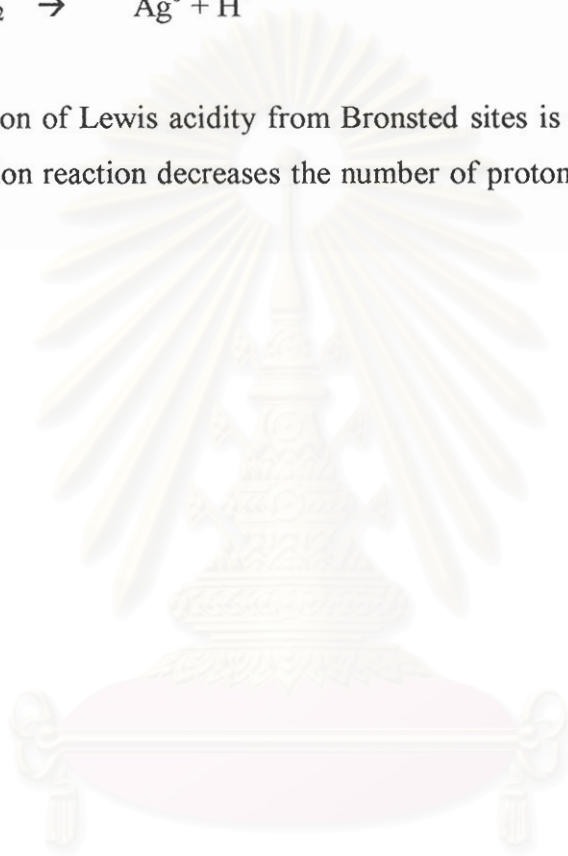


Thus, water molecules coordinated to polyvalent cations are dissociated by heat treatment to give the following local structure in Fig. 3.7.

Bronsted acid sites are also generated by the reduction of transition metal cation. The concentration of OH groups of zeolite containing transition metals was noted to increase by reduction with hydrogen at 250-450°C and to increase by reduction with the rise of the reduction temperature [26].



The formation of Lewis acidity from Bronsted sites is depicted in Figure 3.8 [26]. The dehydration reaction decreases the number of protons and increases that of Lewis sites.



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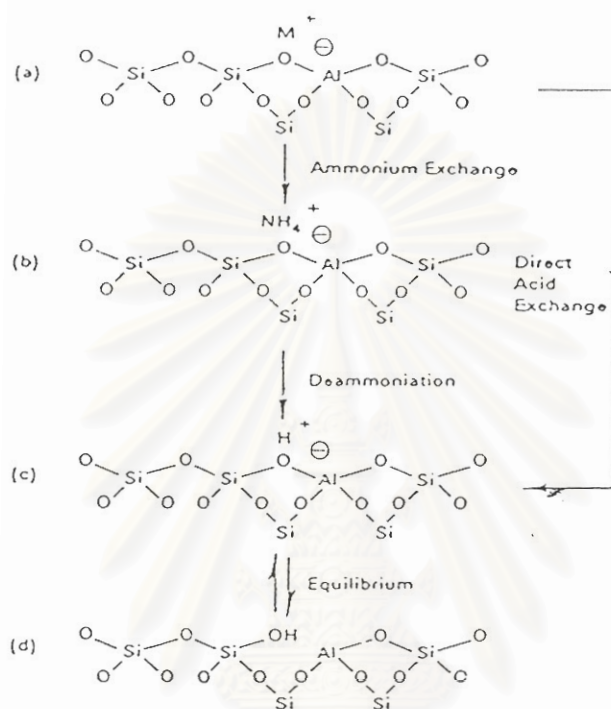


Fig. 3.6 Diagram of the surface of zeolite framework [27]

- In the as-synthesized form, M^+ is either an organic cation or an alkali metal cation.
- Ammonium in exchange produces the NH_4^+ exchanged form.
- Thermal treatment is used to remove ammonia, producing the H^+ acid form.
- The acid form in (c) is in equilibrium with the form shown in (d), where there is a silanol group adjacent to a tricoordinate aluminum.

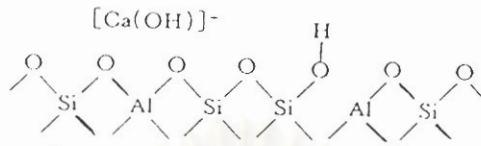


Fig. 3.7 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [26].

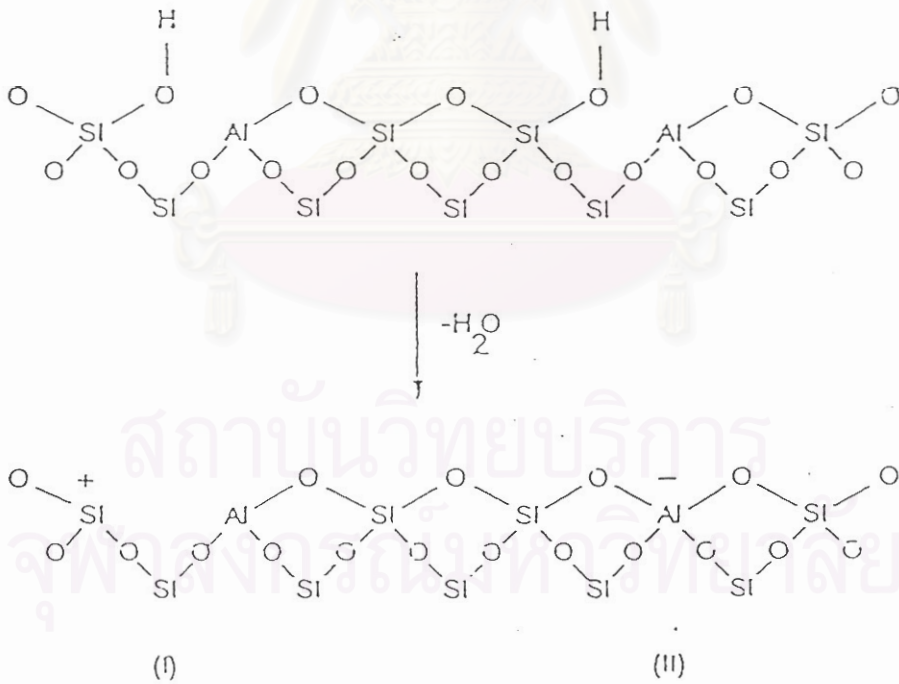


Fig. 3.8 Lewis acid site developed by dehydroxylation of Bronsted acid site [26].

3.2.3) Ion-exchange Reaction in Zeolites

The cation exchange property zeolite minerals were first observed 100 years ago. The ease of cation exchange in zeolites and other minerals led to an early interest in ion exchange materials for use as water softening agents. Synthetic, noncrystalline aluminosilicate materials were primarily used; in more recent years, organic ion exchange resins are used. Crystalline zeolites have not been used commercially as water softeners.

The ion exchange behavior of various inorganic exchangers and other types of crystalline silicates such as clay minerals and feldspathoids have been extensively reviewed. Because of their three-dimensional framework structure, most zeolites and feldspathoids do not undergo any appreciable dimensional change with ion exchange; clay minerals, because of their two-dimensional structure, may undergo swelling or shrinking with cation exchange. One application for commonly occurring zeolite minerals (such as clinoptililite) is in the selective removal of radioactive ions from radioactive waste materials.

The cation exchange behavior of zeolites depends upon (1) the nature of the cation species, the cation size, both anhydrous and hydrated, and cation charge; (2) the temperature; (3) the concentration of the cation species in solution; (4) the anion species associated with the cation in solution; (5) the solvent, most exchange have been carried out in aqueous solutions, although some works have been done in organic solvents); and (6) the structural characteristics of the particular zeolite. Cation selectivity in zeolites does not follow the typical rules that are evidenced by other inorganic and organic exchangers. Zeolite structures have unique features that lead to unusual types of cation selectivity and sieving. The recent structural analyses of zeolites form a basis for interpreting the variable cation exchange behavior of zeolites.

Cation exchange in zeolite is accompanied by dramatic alteration of stability, adsorption behavior and selectivity, catalytic activity and other important physical properties. Since many of these properties depend upon controlled cation exchange with particular cation species, detailed information on the cation exchange equilibrium is important. Extensive studies of the ion exchange processes in some of the more important mineral and synthetic zeolites have been conducted [29].

CHAPTER IV

EXPERIMENTS

4.1) Catalyst Preparation

The parent Na-ZSM-5 zeolite was ALSI-PENTA Zeolithe GmbH, Alustr. 50, 92421 Schwasdorf, Germany, with Si/Al molar ratio of 25. The preparation of Co-ZSM-5 were described as follows:

- Co Loading on Na-ZSM-5 by Ion-exchanged

The Co-ZSM-5 catalysts were prepared by the ion-exchanged method as follows. Approximately 5 g of Na-ZSM-5 was ion-exchanged in an 250 cc, 0.01 M aqueous solution of cobalt(II)acetate as the Co source. The ion-exchanged was performed for 24 h at 80°C under continuous stirring by a magnetic stirrer. After the ion exchange process, the preparation was thoroughly washed with deionized water for 3-5 times to get rid of some ions using centrifuge separator and dried at 110°C for at least 3 hr in an oven. The Co-ZSM-5 catalyst was calcined up to 540°C for 3.5 hr. Quantity of cobalt in zeolites samples were confirmed by AA. Cobalt loading was 1% by weight.

4.2) Nitric Oxide Reduction

4.2.1) Chemicals and Reagents

Nitric oxide (1% by vol.) in helium, Propylene (3% by vol.) in helium, Oxygen of ultra high purity grade (99.999% by vol.) and helium with the same grade as oxygen (99.999% by vol.) were provided by Thai Industrial Gases Limited.

4.2.2) Instruments and Apparatus

A flow diagram of the steady state nitric oxide reduction system is shown in figure 4.1 the system consists of a reactor, an automation temperature controller, an

electrical furnace, a gas control system and a saturator. The instruments used in this system is listed and explained below.

1. Reactor: The NO reduction reactor was a conventional micro-reactor made from quartz tube with 0.6 cm inside diameter. The reaction was carried out under ordinary gas flow and atmospheric pressure. The effluent gas was sampled and analyzed by an on-line gas chromatograph.

2. Automation temperature controller: This unit consisted of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series REX-C900 connected to a thermocouple attached to the catalyst bed in reactor. A dial setting established a set point at any temperature within the range between 0 to 999°C.

3. Electrical furnace: The furnace supplied the required heating to the reactor for NO reduction reaction. The reactor could be operated from room temperature up to 600°C at maximum voltage of 220 volts.

4. Gas controlling system: Nitric oxide, methane, oxygen, and helium cylinders each was equipped with a pressure regulator, and an on-off valve. Needle valves were used to adjust flow rate of gases. A gas-sampling valve was used to take sample of effluent gas.

5. Gas chromatography: The apparatus consist of thermal conductivity detector (TCD) gas chromatographs, SHIMADZU GC8-ATP and SHIMADZU GC-8AIT were used to analyze feed and effluent gas. Operating condition used was shown in table 4.1.

Table 4.1 Operating condition of gas chromatograph

Gas Chromatograph	SHIMADZU GC-8ATP	SHIMADZU GC-8AIT
Detector	TCD	TCD
Packed column	MS-5A	PORAPAK-Q
Carrier gas	He (UHP)	He (UHP)
Flow rate of carrier gas	40 ml/min	80 ml/min
Column temperature	70°C	90°C
Detector temperature	100°C	110°C
Current (mA)	80	90
Analyzed gas	O ₂ , N ₂	C ₃ H ₆ , CO ₂

4.2.3) Procedure

Using a conventional microreactor carried out the catalytic test. The catalyst in powder form was tableted with a tablet machine. It was crushed and sieved to 8-16 mesh to be used for the reaction. A 0.2-g portion of the catalyst was packed in a quartz tube reactor and the catalyst-bed length was about 14 mm. It was heated at room temperature to 500°C for 1 hr under He stream (70 cm³/min), held at this temperature for 1 hr, and then cooled down to room temperature. A gas mixture containing NO (1000-ppm), C₃H₆ (2000-ppm), O₂ (10-vol%) and He balance was fed at a total flow rate of 100 cm³/min (GHSV ≈ 20000 h⁻¹). The reaction gas was introduced at temperature range from 150 to 600°C. The samples of reaction and product gases were taken for the concentration measurement. The gas samples were analyzed by using gas chromatograph with molecular sieve-5A (for O₂, N₂, and CO) columns. The gas chromatograph was equipped with Shimadzu C-R6A integrator. The concentrations of C₃H₆ before and after reaction were analyzed for C₃H₆ consumption. The conversion of NO was calculated based on the concentration of N₂ formed.

4.3) Adsorption, Temperature Programmed Desorption and Temperature Programmed Oxidation Experiments

4.3.1) Adsorption Experiments

The adsorption experiments were conducted to test the mechanism of intermediates formation of NO selective catalytic reduction with propylene over Co-ZSM-5. The instruments and apparatus were the same as nitric oxide reduction experiment. Using a conventional microreactor carried out the catalytic test. The catalyst was tabletted and packed as described above. It was heated at room temperature to 500°C and held at this temperature for 1 hr under He stream (70 cm³/min), Subsequently it was cooled down to room temperature. Gas mixtures were introduced between three gas species of NO (1000-ppm), C₃H₆ (2000-ppm), O₂ (10-vol%) and He balance. The total flow rate of the selected mixture was 100 cm³/min and GHSV ≈ 20000 h⁻¹. The gas mixture was introduced at temperature 100°C. To take up the concentration measurement, the gas samples were analyzed by using gas chromatograph 8-AIT with PORAPAK-Q (for C₃H₆) column. The gas chromatograph was equipped with Shimadzu C-R6A integrator. From the amount of adsorption, the concentrations of C₃H₆ were analyzed from C₃H₆ consumption.

4.3.2) Temperature Programmed Desorption (TPD)

After adsorption experiment. It was continuously followed by the temperature programmed desorption to eliminate the weakly adsorbed or physical adsorbed in the same apparatus. First, the reactant gas was switched off and the inlet gas was He 100 cc/min. Then the reactor was heated with the heating rate of 10°C/min from 100-600°C.

4.3.3) Temperature Programmed Oxidation (TPO)

After desorption, it was continuously followed by the temperature programmed oxidation experiment to test the effect of the mixture of oxidizing agents on deposit intermediates. First, the reactor was cooled down to 100°C. Then the

oxidizing gas mixture was fed. The oxidizing gas mixtures, a total flow rate of 100 cm³/min (GHSV \approx 20000 h⁻¹) in Helium, were O₂ (1 vol%) and/or NO (1000 ppm). Then the reactor was heated with the heating rate of 10°C/min from 100-800°C. To take up the concentration measurement, the gas samples were analyzed by using gas chromatograph GC-8ATP (for detected N₂) and GC-8AIT (for detected CO₂). From the area of CO₂ and N₂, the concentrations of CO₂ and N₂ from reactor outlet were calculated with calibration equation analyzed from C₃H₆ consumption.

4.4) Time-On-Stream Experiment

The effect of time-on-stream experiment was conducted at the reaction temperature of 400°C and 550°C. It was result in catalytic activity. The instruments and apparatus were the same as nitric oxide reduction experiment. Using a conventional microreactor carried out the catalytic test. The catalyst was tabletted and packed as described above. It was heated at room temperature to 500°C for 1 hr under He stream (70 cm³/min), held at this temperature for 1 hr, and then cooled down to room temperature. The reaction gas mixture was NO (1000-ppm), C₃H₆ (2000-ppm), O₂ (10-vol%) and He balance was fed at a total flow rate of 100 cm³/min (GHSV \approx 20000 h⁻¹). For the time-on-stream experiment, it begin with the reaction gas at 550°C. To check the NO conversion to N₂ with GC, the N₂ product was collected at the outlet of reactor. When N₂ concentration was constant, the reaction was switch off. And then it was cooled down to the temperature of 400°C. After that, the reaction gas was switch on again. This test was similar to the test of 550°C. When finished this test, it was switch off the mixed gas and heated upto 550°C again. Finally, it was switch on the mixture of reaction gas. It was taking into N₂ concentration from GC. The reaction was stopped when N₂ concentration was stable.

CHAPTER V

RESULTS AND DISCUSSION

5.1) Time-On-Stream (TOS)

Figure 5.1 was the graph of time-on-stream experiment. The procedure of time-on-stream experiment was described in chapter v and the result was ascribed as follows. At the beginning step, the reaction of reactant gas mixture (1000 ppm NO + 2000 ppm C₃H₆ + 10% O₂) was taken at 550°C. It is obvious that the N₂ concentration detected from reactor outlet which refers to the NO conversion, gradually decreases from 0 minute to 30 minute and then the conversion remains constant value. It was subsequently switched off the reaction gas and cooled down the reaction temperature to 400°C. Next, the reaction gas was switched to the reactor at this temperature. It is observed that the N₂ product diminishes as a function of time. Interestingly, it is close to zero with in 1 hour. After that, the reaction gas was switched off and the reaction temperature was heated up to 550°C. Like the above experiment, the reactant was introduced to the reactor at the temperature of 550°C again. It is found that initial N₂ product is much higher in the latter than in the earlier. Then, the N₂ product decreases with time. For a longer time, the N₂ product is constant value, which is similar to the concentration of N₂ product in the first run of 550°C.

This result was deal with NO conversion in the SCR of NO with hydrocarbon in the presence of excess of oxygen. The decrease of N₂ concentration as well as NO conversion was due to the carbon deposits effect. At the temperature of 550°C, the initial decrease of NO conversion may be due to the deposits that deposited on the clean surface of catalyst. After that, the NO conversion seems to be constant, this can imply that after the initial deposition of deposits, the deposits can not deposit any more because at this temperature, it was high enough to avoid the accumulation of deposits. At the temperature of 400°C, NO conversion decreased with time on stream. After 1 hour, it was disappeared. This may be implying that the deposits, which can not remove in this temperature, suppress the NO reduction. This is corresponding with Chen *et al.* They observed the decrease of NO conversion at 300°C as a function of time-on-stream for Fe-ZSM-5 in the NO selective catalytic reduction with i-C₄H₁₀ and n-C₄H₁₀. They suggested that the deactivation was accounted for the formation of as

active deposits [38]. Significantly, the deposits blocked sites of NO adsorption. Thus, the reaction, which is catalyzed by the iron sites, will be hindered [39]. Compared the initial NO conversion between the first test and the last test at 550°C, it was seen that the last test was the much greater conversion than the first test. This can be implied into two cases. In the first cases, the deposits, kinds of intermediates, can react with reactant gas to produce N₂ product. The other case, deposits can self-decompose to N₂ product when the reaction temperature is high enough. Furthermore, this is in accordance with Walker [40]. He mentioned that the carbonaceous deposits merely acted as reductant for impinging NO or NO₂. From this result, carbon deposits are reversible poisons. If the reaction temperature is high enough for removing them, the NO reduction activity can be recovered.

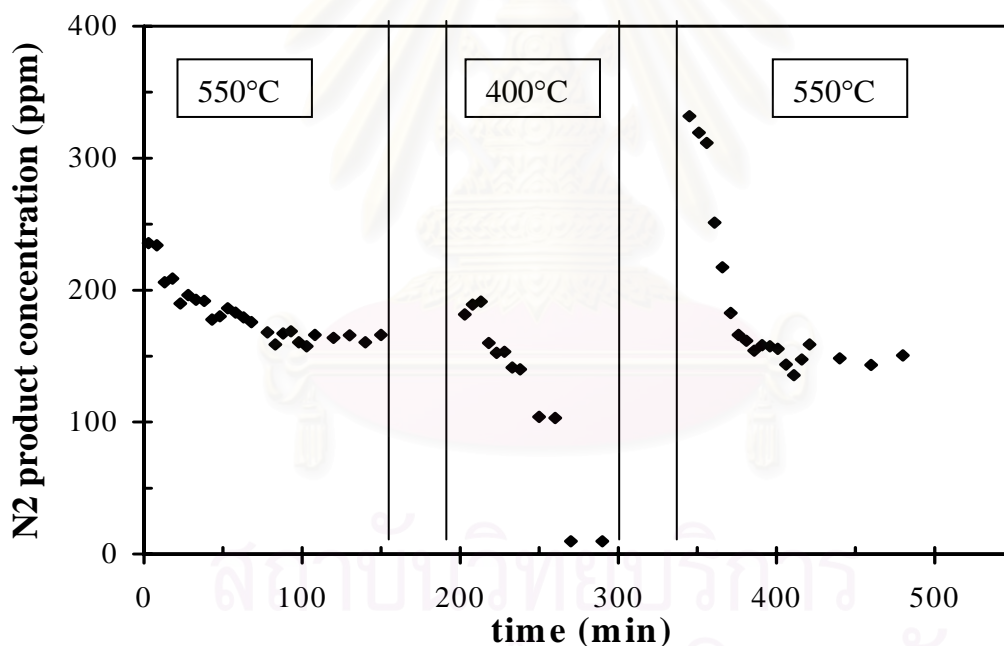


Figure 5.1 N₂ product concentration from reactor outlet as a function of time on stream of Co-ZSM-5 at Temperature 550°→ 400°C→550°C, [NO] = 1000 ppm, [C₃H₆] = 2000 ppm, [O₂] = 10 %, 0.2 g Co-ZSM-5, GSHV ≈ 20000 h⁻¹

5.2) Effect of Hydrocarbon Species on Selective Catalytic Reduction of NO with Hydrocarbon

In this section, the adsorption and reaction experiments were conducted with two hydrocarbon species of propane and propylene over Co-ZSM-5, Cu-ZSM-5 and H-ZSM-5 catalysts. The adsorption results are displayed in figures 5.2, 5.3 and 5.4. The results show that propylene is more significantly adsorbing than propane in all catalysts, result in higher adsorbed species. Therefore, it can imply that the nature of deposits is depending on type of hydrocarbon. The high deposits formation occurs in the case of propylene, contrary to propane that can not form deposits adsorbed on the catalyst surface. On the other hand, figures 5.5, 5.6 and 5.7 illustrate NO conversion of these three catalysts (Co-, Cu-, and H-ZSM-5). The results indicate that NO conversion of reactions using propylene as reductant occurs in higher temperature region than using propane as reductant.

Obviously, NO conversion of propane and propylene are less different for Cu-ZSM-5 catalyst (figure 5.6) than for Co-ZSM-5 and H-ZSM-5 catalysts (figures 5.5 and 5.7). Compared with the two other catalysts, the reaction of propylene over Cu-ZSM-5 occurs in the lower temperature range. In addition, it was also considerable difference in the TPO results of Co-ZSM-5 and Cu-ZSM-5 exhibited in figure 5.8. It is noticed that deposits on Cu-ZSM-5 can be easier removed in lower temperature than Co-ZSM-5. It may owe the intermediate deposits on SCR reaction. As the conclusion of time-on-stream experiment that mention the suppression of NO conversion activity by deposits accumulation. Also, the conclusions of these experiments are the formation of intermediates depending on the type of hydrocarbons that can affect significantly on SCR reaction and the unremovable deposits at a temperature can suppress the NO reduction reaction. According to Chen [39], he mentioned that the rate-limiting step in NO_x reduction depends on the nature of the hydrocarbon. This is associate with our results.

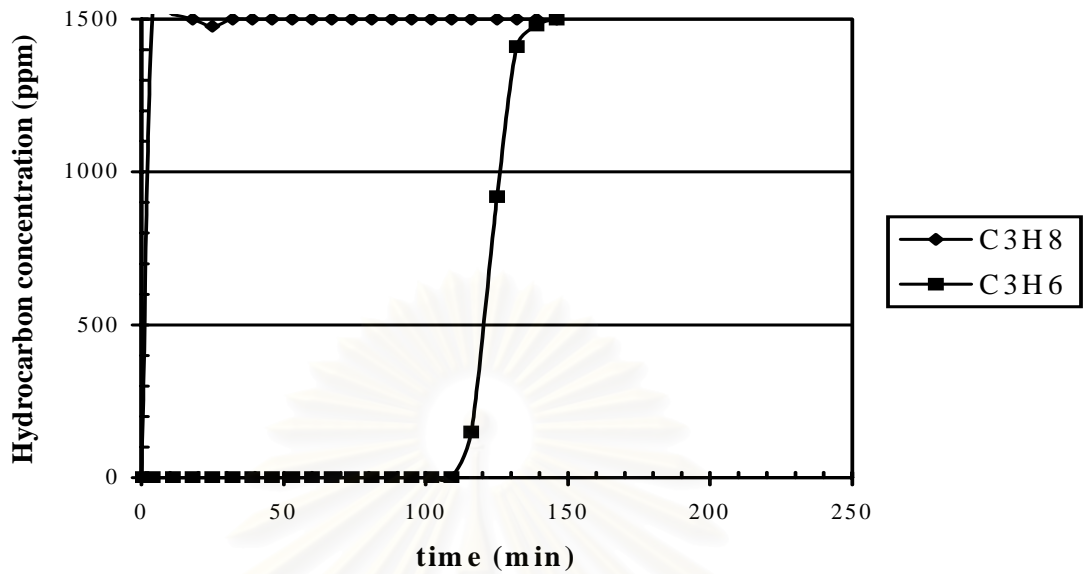


Figure 5.2 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment on Co-ZSM-5 at 100°C, [C₃H₆ or C₃H₈] = 1500 ppm in He balance 100 cc/min, 0.7 g Co-ZSM-5

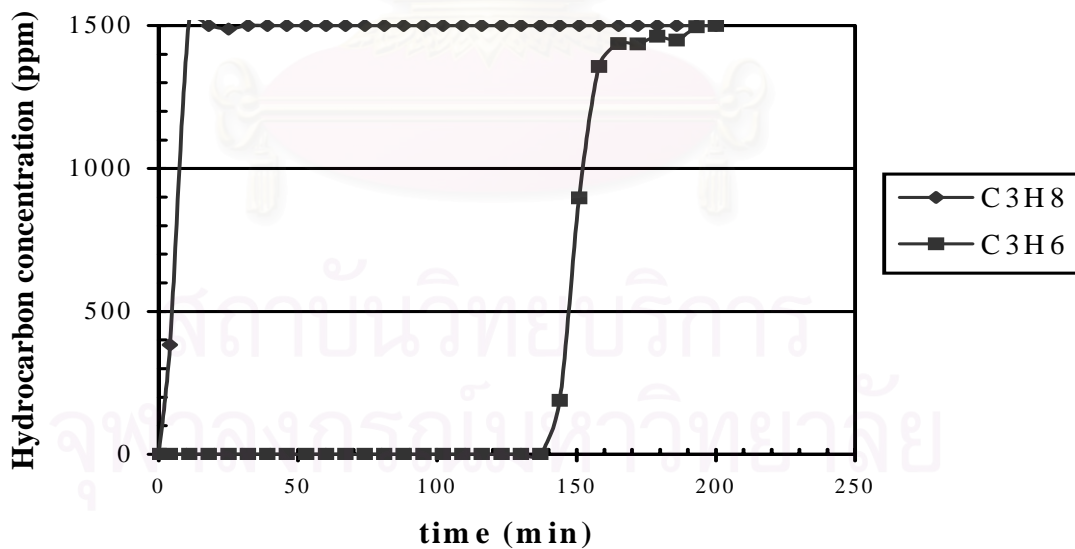


Figure 5.3 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment on Cu-ZSM-5 at 100°C, [C₃H₆ or C₃H₈] = 1500 ppm in He balance 100 cc/min, 0.7 g Cu-ZSM-5

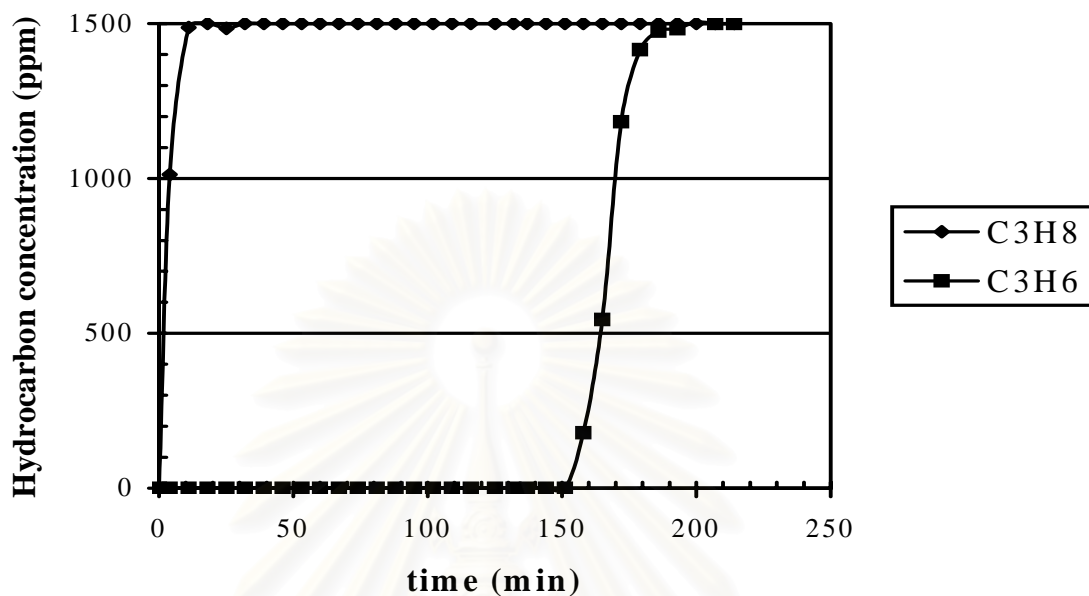


Figure 5.4 Hydrocarbon concentration from reactor outlet of hydrocarbon adsorption experiment at 100°C (C₃H₆, C₃H₈) = 1500 ppm in He balance 100 cc/min, 0.7 g H-ZSM-5

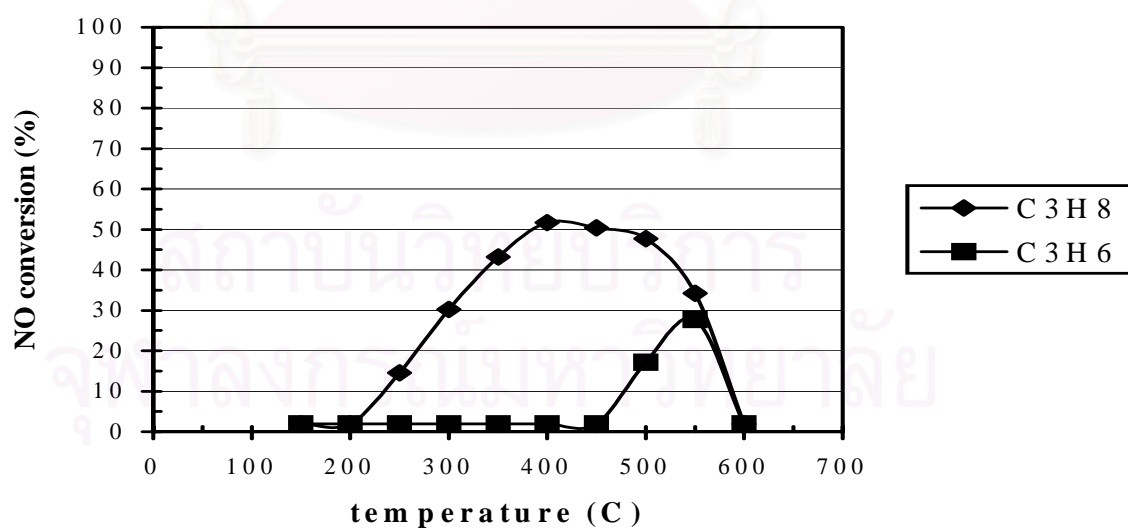


Figure 5.5 NO conversion as a function of temperature and hydrocarbon on Co-ZSM-5, [NO] = 1000 ppm, [C₃H₆ or C₃H₈] = 2000 ppm, [O₂] = 10 %, GSHV \approx 20000h⁻¹

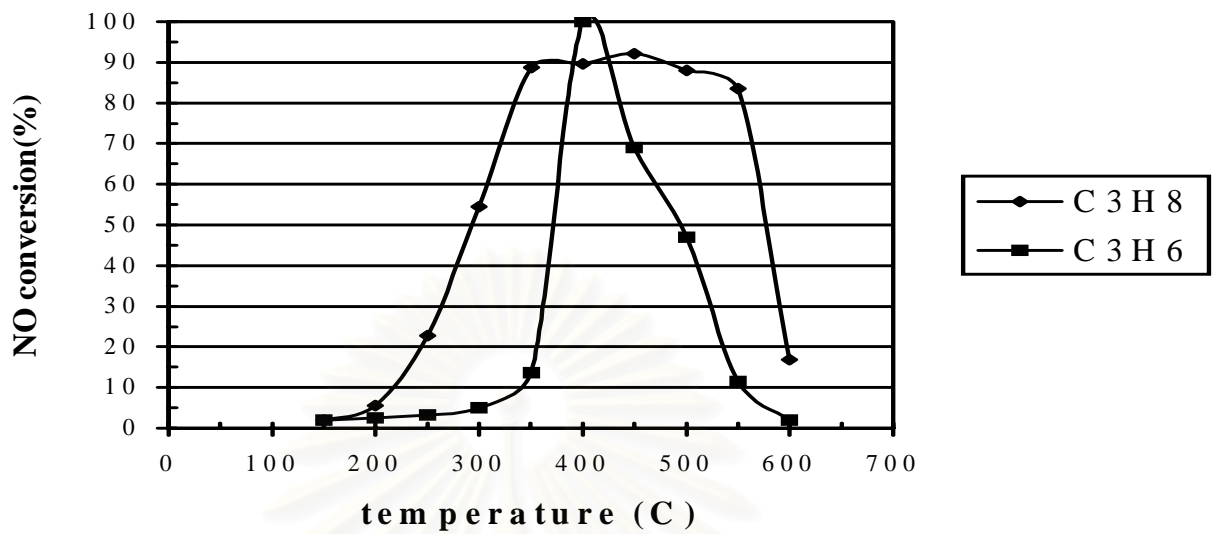


Figure 5.6 NO conversion as a function of temperature and hydrocarbon on Cu-ZSM-5, [NO] = 1000 ppm, [C₃H₆ or C₃H₈] = 2000 ppm, [O₂] = 10 %, GSHV ≈ 20000h⁻¹

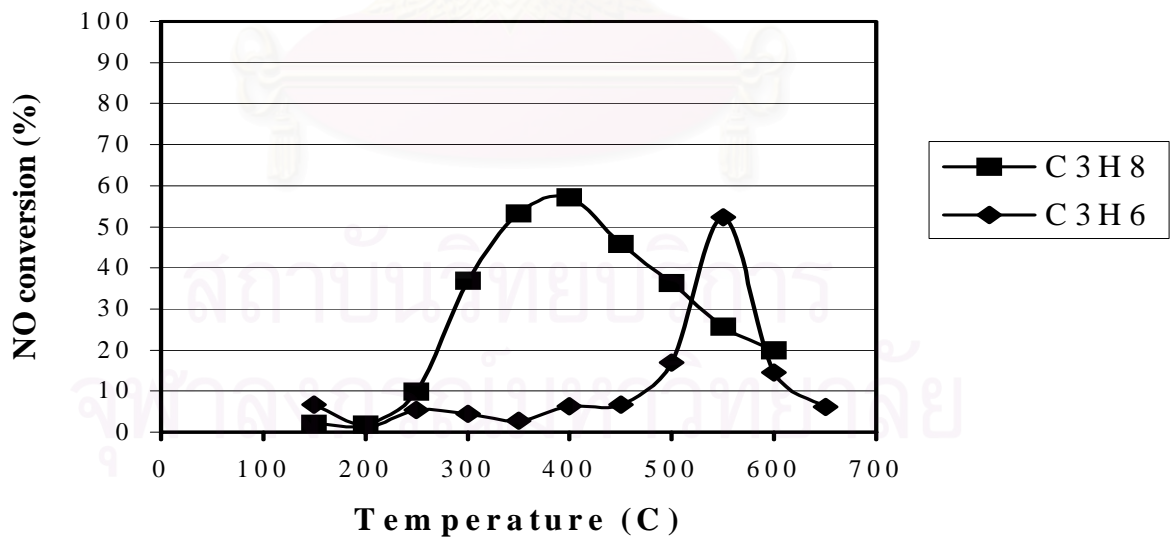


Figure 5.7 NO conversion as a function of temperature and hydrocarbon on H-ZSM-5, [NO] = 1000 ppm, [C₃H₆ or C₃H₈] = 2000 ppm, [O₂] = 10 %, GSHV ≈ 20000h⁻¹

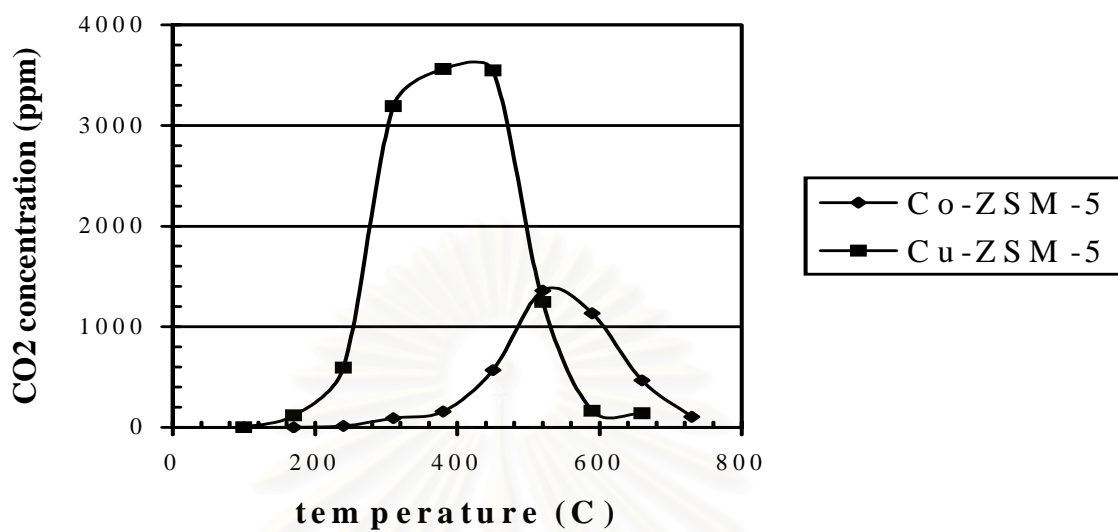


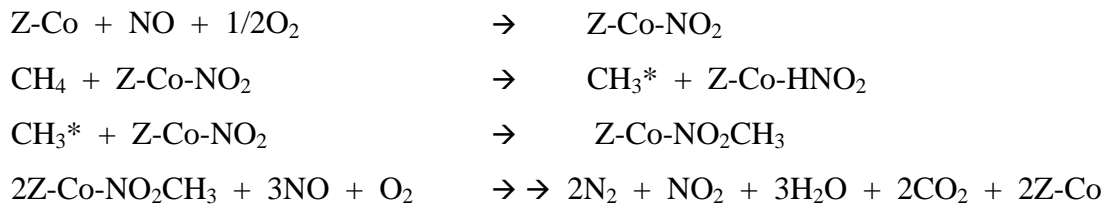
Figure 5.8 CO₂ concentration from reactor outlet of temperature programmed oxidation by O₂ experiment on Co- and Cu-ZSM-5 after adsorption of propylene = 2000 ppm in He balance 100 cc/min, 0.7 g Catalysts

5.3) Study of Intermediate Formation by Variation of Adsorbed Gas Mixtures

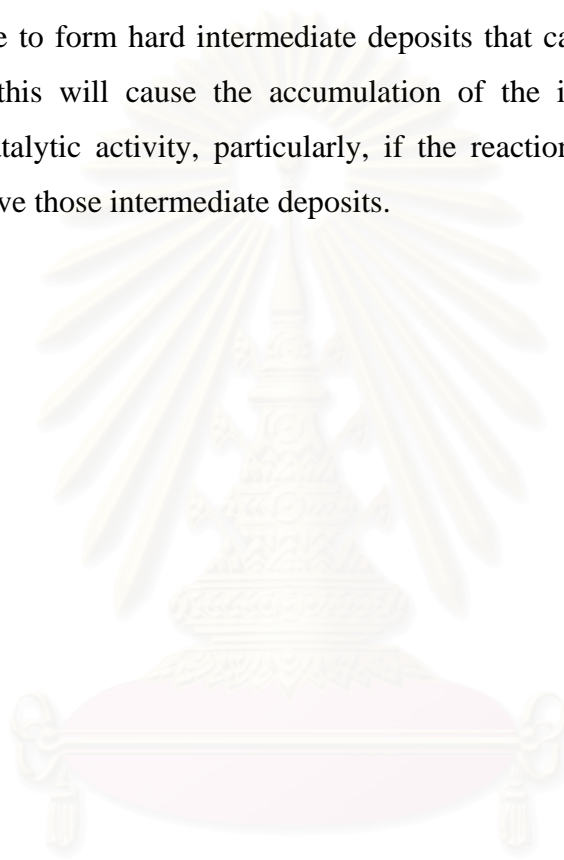
TPO spectra observed over the catalysts after being adsorbed by four gas mixtures ($C_3H_6+NO+O_2$, C_3H_6+NO , $C_3H_6+O_2$, C_3H_6) at $100^\circ C$ on Co-ZSM-5 until the adsorption was stopped (the propylene concentration from the reactor outlet was constant) and desorbed at higher temperature ($100 - 600^\circ C$) are illustrated in figures 5.9 and 5.10.

Figure 5.9 shows that only the adsorbed gas mixture of $C_3H_6+NO+O_2$ formed a significant amount of intermediate deposits, whereas the other gas mixtures resulted in a little amount of deposits. This result can imply that the most possible part of intermediates forming step of the HC-SCR of NO is the corporation of the three reactant gas species (NO, C_3H_6 , and O_2).

Considering figure 5.10, where N_2 concentrations from reactor outlet of temperature programmed oxidation (by O_2) experiment on Co-ZSM-5 after adsorption experiment by varying gas mixtures and desorption (the same experiment as figure 5.9) were plotted versus temperatures, it is seen that N_2 would emerge only from the system that consisted of O_2 . This implies that the adsorbed intermediates in SCR reaction are formed by the interaction of C_3H_6 , NO and O_2 . The results are correspondent with the literatures. Chang *et al.* [41] found that co-adsorption of NO and O_2 led to a substantial increase in the amount of NO_x adsorbed. Similar behavior was reported over Co-ZSM-5 catalyst (Sun *et al.* [22]) where NO was hardly adsorbed in the reaction temperatures, but the interaction between NO and Co cations was greatly enhanced in the presence of O_2 . In addition, Pinaeva *et al.* [42] suggested that over Co-ZSM-5, Co ion located at the interface of Co clusters and zeolites were found to react with NO in the presence of O_2 to form anchored NO_2 delta+ species stabilized under reaction conditions. Therefore, it can be proposed that the initial step of the NO-SCR reaction with hydrocarbon reductant in the presence of excess oxygen over Co-ZSM-5 catalyst is the adsorption of NO_y species formed by the interaction with NO and O_2 . Then NO_y species will interact with hydrocarbon and form nitrogen-containing deposits which are the intermediates of the reaction. However, the formation of intermediate species depends mainly on hydrocarbon reductant and influences the reaction activity. In case that CH_4 is used, the intermediates are the compositions formed by CH_4 free radical as proposed by Li *et al.* [33]:



And for other hydrocarbons, there will be the different intermediates that effect the activity of SCR reaction. If use long chain hydrocarbon or double bond hydrocarbon that more active to form hard intermediate deposits that can hardly react forward to form product, this will cause the accumulation of the intermediate deposits that suppress the catalytic activity, particularly, if the reaction temperature is not high enough to remove those intermediate deposits.



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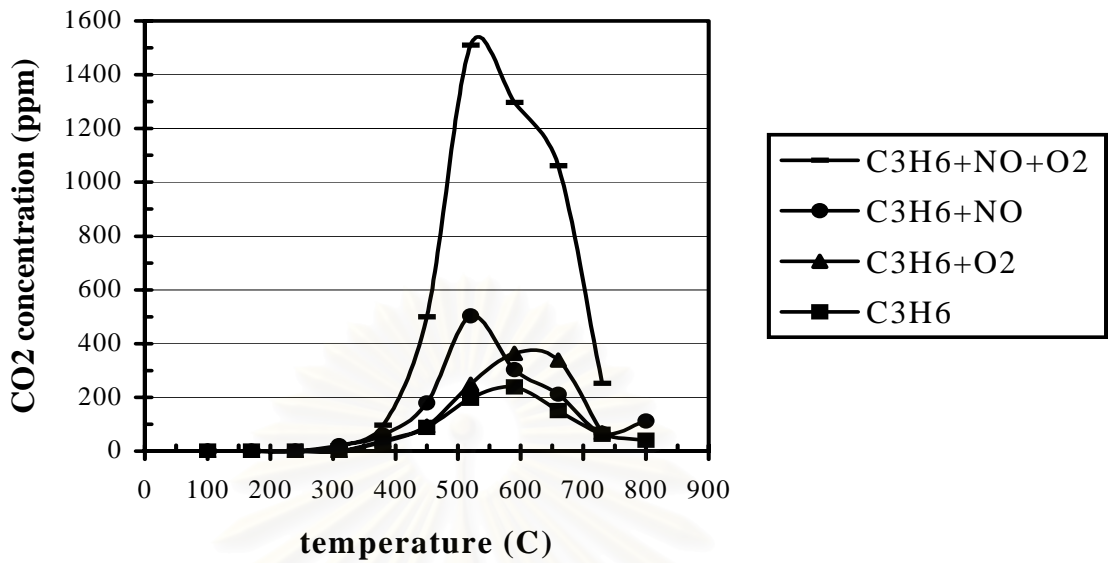


Figure 5.9 CO₂ concentration from reactor outlet of temperature programmed oxidation by O₂ experiment on Co-ZSM-5 after adsorption experiment by varying gas mixtures and desorption

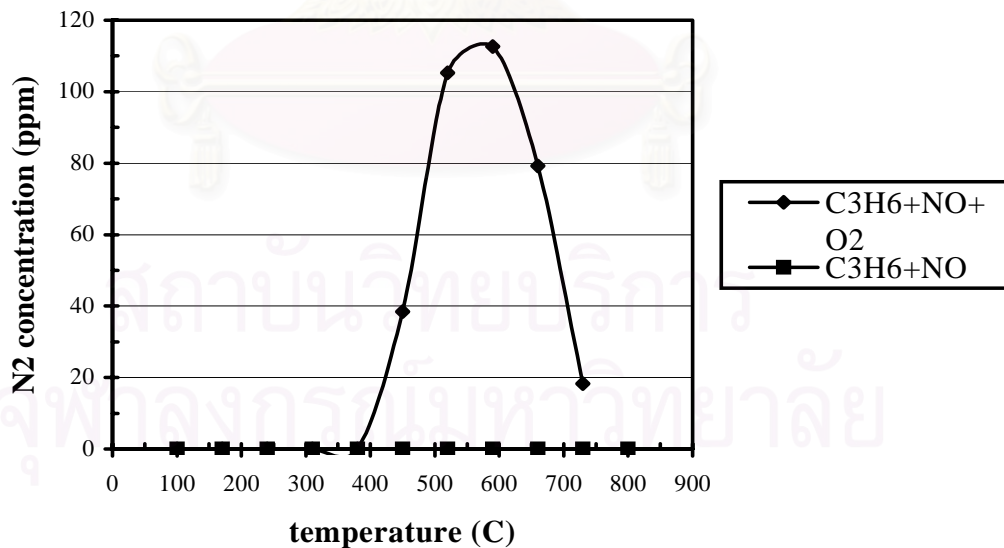


Figure 5.10 N₂ concentration from reactor outlet of temperature programmed oxidation by O₂ experiment on Co-ZSM-5 after adsorption experiment by varying gas mixtures and desorption

5.4) Study of Intermediates Removal by Varying Oxidizing Gas Mixture

In order to study the mechanism of intermediates removal in the SCR of NO_x with propylene in the presence of excess oxygen over Co-ZSM-5, TPO experiments by varying oxidizing gas mixtures (O_2 , NO and $\text{NO}+\text{O}_2$) was conducted on Co-ZSM-5 catalyst after being adsorbed by a gas mixture of $\text{C}_3\text{H}_6+\text{NO}+\text{O}_2$ at 100°C and desorbed at higher temperature ($100 - 600^\circ\text{C}$). The results show in figure 5.11 and 5.12.

As seen in figure 5.11, a little amount of CO_2 was emerged from the effluent gas when only NO was used as the oxidizing gas. On the other hand, large amount of CO_2 was shown when the oxidizing agent was O_2 or the mixture of NO and O_2 . These results imply that the deposits removal reaction is effectively occurred in the presence of oxygen. Interestingly, when a gas mixture of NO and O_2 was used instead of O_2 alone, the deposit removal reaction would occur at lower temperature region. Therefore, it can be concluded that the incorporation of NO and O_2 accelerate the intermediates removal reaction.

Although the amount of CO_2 emerged from the effluent gas between TPO by O_2 and TPO by $\text{NO}+\text{O}_2$ was not much different, the N_2 concentrations in both cases were remarkably different as illustrated in figure 5.12. TPO by $\text{NO}+\text{O}_2$ resulted in larger amount of N_2 emerged and N_2 emerged at lower temperature. This result implies that the increased amount of nitrogen may be attributed to nitrogen in gas phase (from NO feed) that can interact with intermediate deposits and form nitrogen products. Thus, nitrogen products observed were from both nitrogen-containing intermediate deposits and nitrogen from gas phase. This is in agreement to the results show before and the literature of H. Y. Chen *et al.* [39] which uses isotopic labeling technique on Fe-ZSM-5 and found that one nitrogen atom in every nitrogen produced come from the deposits, the other comes from gas phase NO_2 .

In addition, from figure 5.12, N_2 was emerged at high temperature. However, such amount of N_2 may not be occurred from the intermediate deposits since there was no CO_2 produced at the same temperature (see figure 5.11). It is believed that this detected nitrogen may be caused by the NO decomposition, which occurs at very high temperature and need no O_2 . This result is correspondent with the observation by Wang *et al.* [43] that NO was reduced in O_2 -free feed over Co-ZSM-5 at high

temperature, suggesting that NO can be reduced over Co^{2+} ion without the intermediates formation of NO_2 .

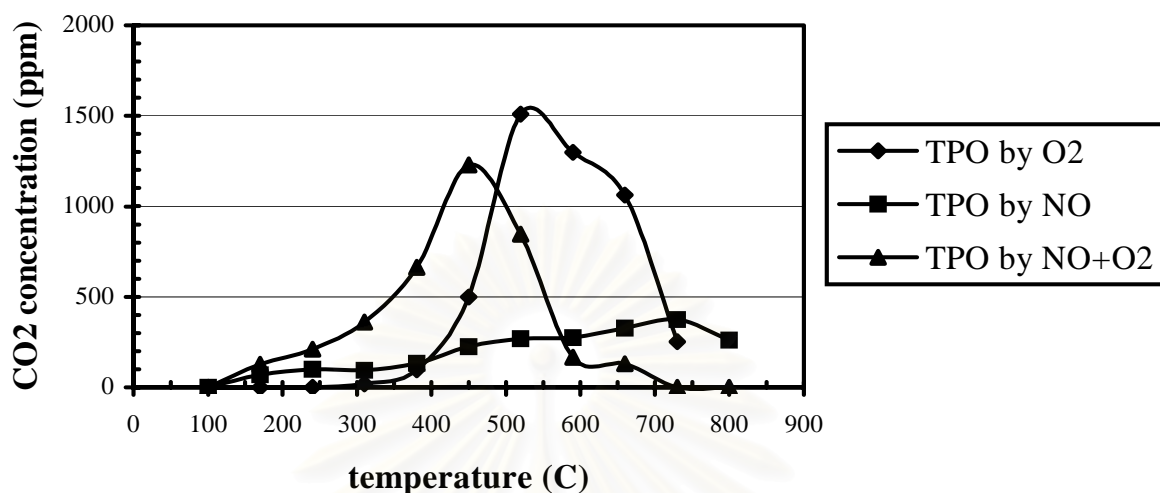


Figure 5.11 CO_2 concentration from reactor outlet of temperature programmed oxidation by varying oxidizing gas mixtures on Co-ZSM-5 after adsorption by $[\text{NO}] = 1000$ ppm, $[\text{C}_3\text{H}_6] = 2000$ ppm, $[\text{O}_2] = 10\%$, 0.2 g Co-ZSM-5, GSHV ≈ 20000 h^{-1}

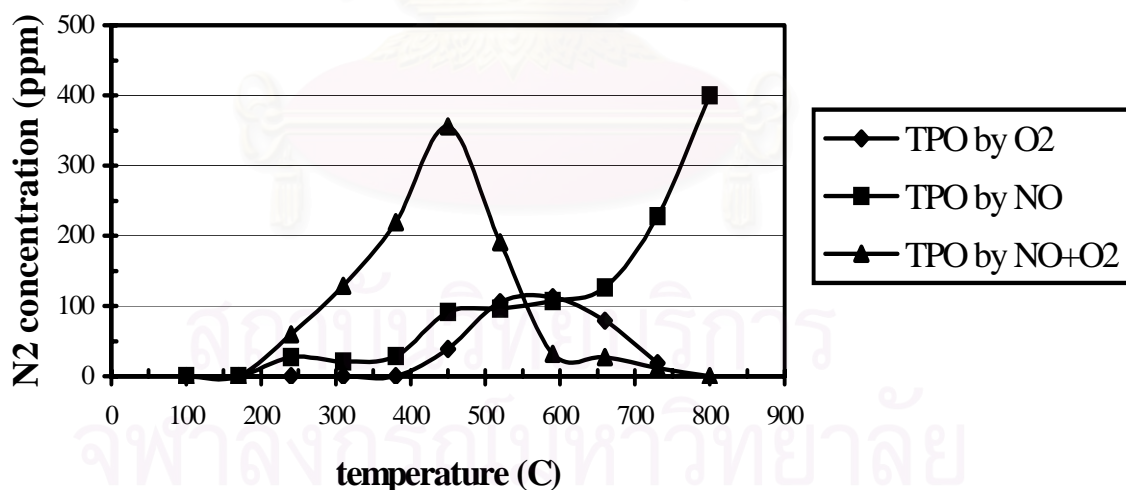


Figure 5.12 N_2 concentration from reactor outlet of temperature programmed oxidation by varying oxidizing gas mixtures on Co-ZSM-5 after adsorption by $[\text{NO}] = 1000$ ppm, $[\text{C}_3\text{H}_6] = 2000$ ppm, $[\text{O}_2] = 10\%$, 0.2 g Co-ZSM-5, GSHV ≈ 20000 h^{-1}

5.5) The Influence of Adsorption Time on Deposits

The adsorption experiments were carried on a gas mixture of C_3H_6 , NO and O_2 at $400^\circ C$ with various adsorption time (10, 30, 90 and 390 minutes). The influences of time on amounts of carbon, nitrogen and nitrogen per carbon ratio of deposits were demonstrated in figures 5.13, 5.14 and 5.15, respectively. It was seen that they had the same trend. Initially, the amounts of carbon, nitrogen and N/C ratio increase rapidly and then they decrease after 100 minutes. These may result from the deposits formation. In the first period, the deposits were sharply appeared since the catalyst surface was still clean. Hence, the gas reactants can easily reach the active site to form deposits. In contrast to the longer time, active sites of the catalyst surface were covered by the deposits, thereby, decreasing deposits formation.

5.6) The Influence of Adsorption Temperature on Deposits

Figure 5.16, 5.17 and 5.18 show influence of temperature on amounts of carbon, nitrogen and N/C ratio of deposits, respectively. The temperature conditions were $100^\circ C$, $200^\circ C$, $300^\circ C$ and $400^\circ C$ for the adsorption experiments in the same adsorption time of 90 minutes. Considering figures 5.16 and 5.17, the amounts of carbon and nitrogen on deposits increase with adsorbed temperature, whereas above the temperature of $300^\circ C$ they decrease. The higher temperature increases, the greater deposits formation occurs. Also the higher temperature affects on the increase of deposits remove. Consequently, the effect of temperature was significantly influenced on the formation and remove of deposits. In fact, the deposits formation can form at the low temperature to high temperature, however, the deposits remove is mostly occurred at high temperature.

On the other hand, the influence of temperature on N/C ratio of deposits was exhibited in figure 5.18. It is noticed that the N/C ratio decreases with increasing temperature. It is relevant to the nature of deposits. It is indicated that the softer deposits are associated with the higher N/C ratio, while the harder deposits are associated with the lower N/C ratio. This is mentioned in the previous work [38]. As reported above, at higher temperature, the deposits must hard enough to be not removed by decrease their N/C ratio called hard deposits.

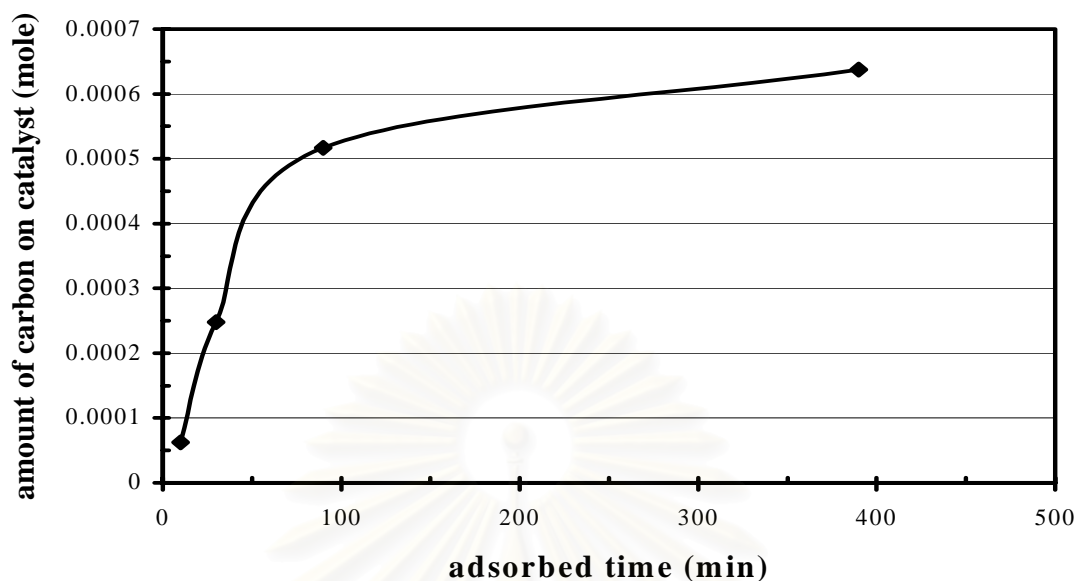


Figure 5.13 Amount of Carbon on Catalyst (mole) as a function of adsorbed time (minute), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, He balance 100 cc/min, 0.2 g Co-ZSM-5

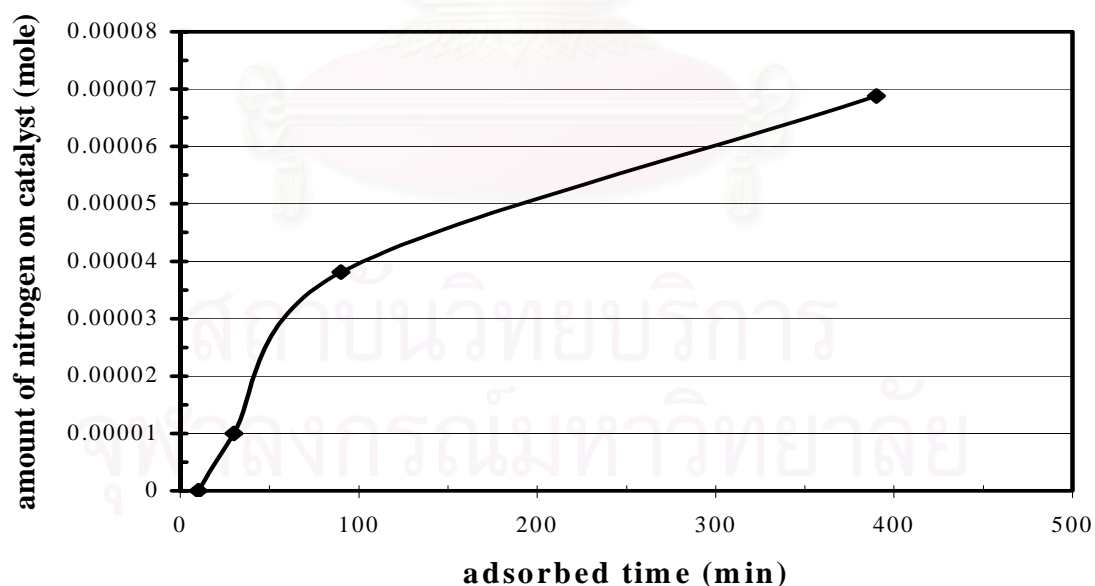


Figure 5.14 Amount of Nitrogen on Catalyst (mole) as a function of adsorbed time (minute), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, He balance 100 cc/min, 0.2 g Co-ZSM-5

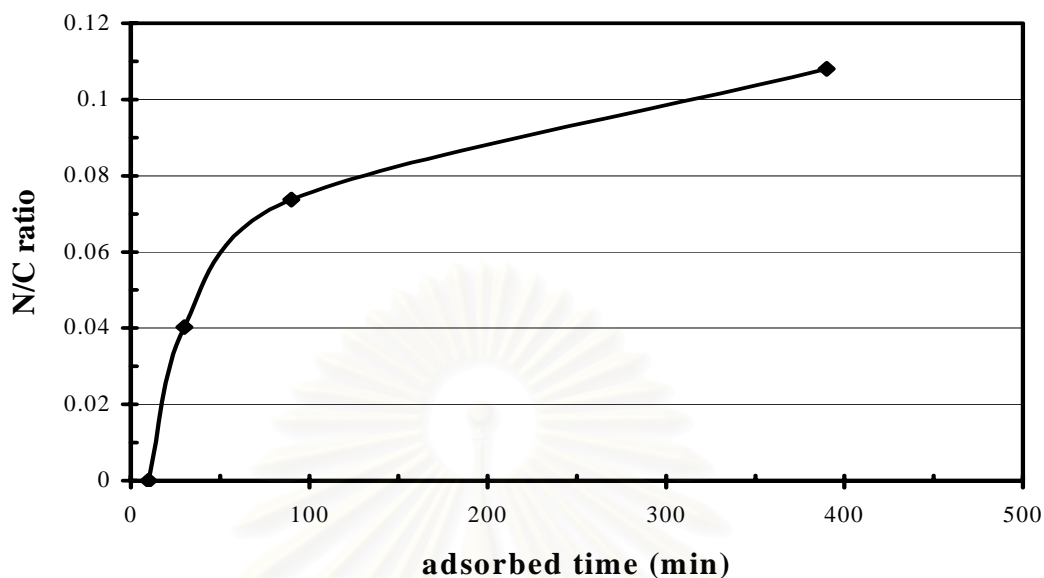


Figure 5.15 N/C ratio as a function of adsorbed time (minute), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, He balance 100 cc/min, 0.2 g Co-ZSM-5

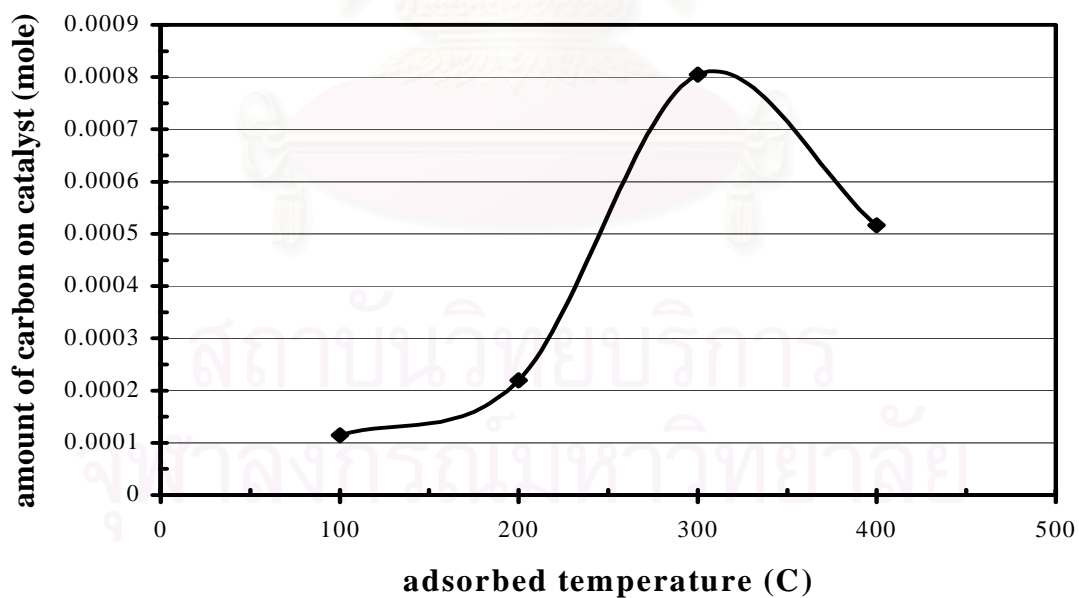


Figure 5.16 Amount of Carbon on Catalyst as a function of adsorbed temperature (C), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, He balance 100 cc/min, 0.2 g Co-ZSM-5

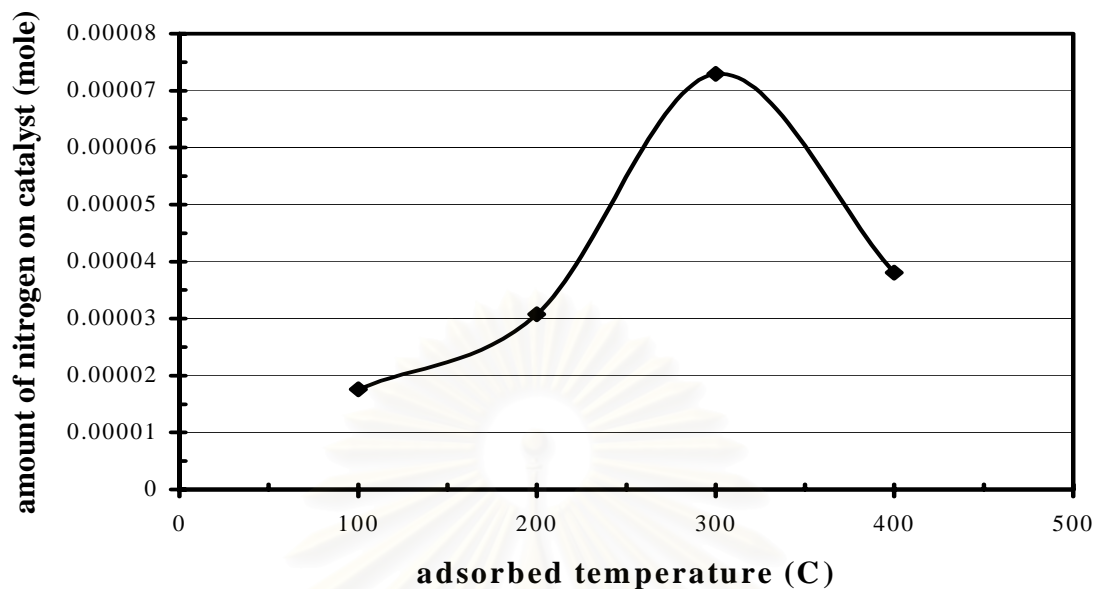


Figure 5.17 Amount of Nitrogen on Catalyst as a function of adsorbed temperature (C), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, 100 cc/min, 0.2 g Co-ZSM-5

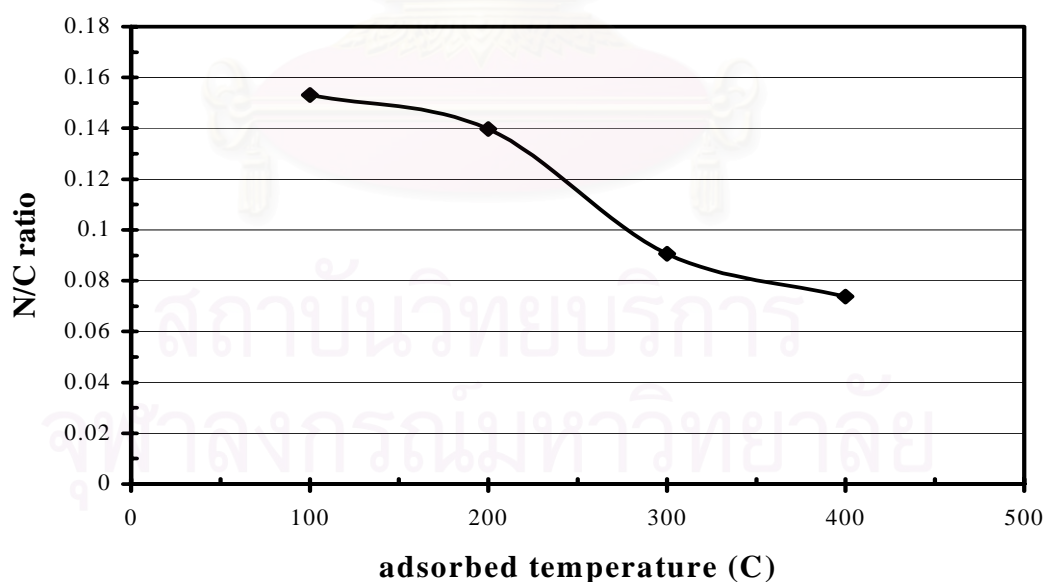


Figure 5.18 N/C ratio as a function of adsorbed temperature (C), adsorbed gas mixture: 1000 ppm NO, 2000 ppm C₃H₆, 10% O₂, He balance 100 cc/min, 0.2 g Co-ZSM-5

5.7) Mechanism of the Selective Catalytic reduction of NO with hydrocarbon over Co-ZSM-5

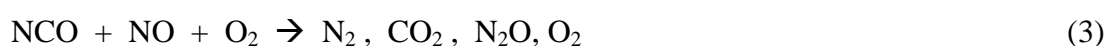
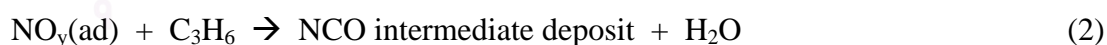
From literature of Misono [4], it mentions that the mechanism proposed so far are divided into three major classes. And from many literatures that involved the mechanism of NO with hydrocarbon [4, 22, 32, 33, 35, 36, 37, 39, 46], as describe in literatures review. There can be concluded that the mechanism was involving adsorbed NO_2 formation by NO and O_2 , which then reacts with hydrocarbon to form intermediate deposits on Co ion. Then the intermediate deposits are oxidized by NO and O_2 or NO_2 to form nitrogen products.

This thesis studied the mechanism of selective catalytic reduction of NO with propylene in the presence of excess oxygen over Co-ZSM-5. The results from this work show that the intermediates formation is occurs in the gas mixture of $\text{C}_3\text{H}_6+\text{NO}+\text{O}_2$ more than other cases (from figure 5.9 and 5.10). Then, the mechanism involving the activation of hydrocarbon by oxygen forming intermediates are not the main reaction step in this reaction, this is a similar scheme as discussed in literatures review. And the results in figures 5.11 and 5.12 show that NO can be oxidized above 700°C in the presence of deposits, so the mechanism involving NO decomposition in this reaction would not be the main mechanism. As corresponding with the literature [22] which suggests that the interaction between NO and Co-ZSM-5 was very weak or that equilibrium between NO adsorption and desorption was very rapid, then, this weak adsorption cannot activate NO decomposition. Hence, the main mechanism of the selective catalytic reduction of NO with hydrocarbon over Co-ZSM-5 would be the mechanism that involves the formation of intermediate deposit from adsorbed NO_y on Co-ZSM-5 and hydrocarbon, as corresponding with the discussed in literatures review.

From the results described in issue 5.3 that the intermediate deposits formation occurred in the presence of three reactants ($\text{C}_3\text{H}_6+\text{NO}+\text{O}_2$), on the other hand, the presence of NO and O_2 enhanced the activated hydrocarbon forming deposits. And there are many literatures mentioned the formation of NO_2 from $\text{NO}+\text{O}_2$ [4, 22, 32, 33, 34, 35, 36, 37, 46] (as mentions in literatures review). From the literature of Goryashenko *et al.* [32] which mentioned that the gas phase NO_2 is not involved directly in the SCR reaction, and the speculation of Armor was the surface NO_2 is more important than the gas phase and the decrease of these surface NO_2 species can

be responsible for the decrease of the SCR activity. The formation of NO₂ adsorbed on cobalt cations was also observed in the work of Sun *et al.* [22]. With DRIFT experiments manifested that the chemical nature of cobalt cations in ZSM-5 changed drastically when a gas mixture of NO and O₂ was introduced. The most prominent change was the interaction of Co²⁺ cations with zeolite framework oxygen. Both the disappearance of the preturbed Si(Al)-O band and the emergence of Co-O band upon exposure to a mixture of NO and O₂ indicated that Co²⁺ relaxed its coordination with the zeolite framework in the presence of NO-O₂ mixture, forming some structured NO₂ intermediates in ZSM-5. The creation of NO₂ intermediates in Co-ZSM-5 was further confirmed by the development of bands in the range of 1350-1400 cm⁻¹, which have also been observed in NO₂-containing cobalt salts. The NO₂ intermediate on the surface of Co-ZSM-5 was found to be very stable, and could not be removed by flushing with pure helium at 450°C. Then, it can be suggested that the active species for NO reduction in Co-ZSM-5 were the adsorbed NO₂ intermediates [22]. Hence, the reaction of NO and O₂ forms NO₂ adsorbed on catalyst surface and the formation of intermediates by the reaction of adsorbed NO_y complexes with propylene are proposed.

From the results described in issue 5.4 that the intermediate deposits removal occurred in the presence of O₂ and it was enhanced by the presence of NO. And the nitrogen products were from both nitrogen-containing intermediate deposits and nitrogen from NO feed. Then, the removal mechanism of intermediates are proposed that the intermediates react with NO and O₂ to form nitrogen products. This is corresponding to literatures [4, 22, 32, 33, 35, 36, 37, 39, 46]. Hence, the mechanism of selective catalytic reaction of NO with propylene in the presence of excess oxygen over Co-ZSM-5 are proposed as scheme below.



From the results in issue 5.2, propane was little adsorbed on catalyst surface but the great amounts of deposits were appeared in the case of adsorbed propylene. From figure 5.8, deposits

can formed on Cu-ZSM-5 more than Co-ZSM-5. Hence, there can be implied that the the deposits formation may be influenced by type of loaded cation and type of adsorbed hydrocarbon. The NO conversion in figures 5.5, 5.6 and 5.7, show the difference of reaction activity of the SCR of NO with different hydrocarbon (propane and propylene) and different loaded cation, this indicates that the nature of deposits can greatly affect the NO reduction activity, and also imply that the intermediate deposits removal reaction can be the rate limiting step. From literature involving SCR of NO with methane over Co-ZSM-5 [36], it proved that the reaction of methane and nitric oxide in the presence of oxygen over Co-ZSM-5 catalysts exhibits a substantial deuterium kinetic isotope effect, then the most probable explanation is the the rate determining step involves hydrogen adstraction from methane itself. The results from literature of Lombardo *et al.* shows that the NO conversion of gas mixture $\text{NO} + \text{O}_2 + \text{nitromethane}$ was much higher than the NO conversion of gas mixture $\text{NO} + \text{O}_2 + \text{CH}_4$, this phenomenon can also indicate that intermediates forming reaction may be one of rate-determining step. Whereas in the literature of Chen *et al.* [38] which showed the results of temperature dependence of the N_2 yield using C_3H_8 , $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$ as reductance, the result describes as follow: The temperature at which the maximum N_2 yield shifts upward in the order $\text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10} < i\text{-C}_4\text{H}_{10}$. The maximum N_2 yield is about the same for $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$, but it is lower for C_3H_8 . This shows that propane is a less effective reductant for SCR of NO_x . Whereas in the descending branches above 375°C , the differences in N_2 are less obvious, the N_2 yield in the ascending branches is higher for C_3H_8 and $n\text{-C}_4\text{H}_{10}$ than for $i\text{-C}_4\text{H}_{10}$. This shows that H adstraction from the alkane is not necessarily a rate-limiting step, and the results of this literature also show the difference of deposit that formed from different hydrocarbons and the difference of reaction activity, then it can be concluded that the mechanism of deposits removal may be one of the rate determining step.

The TPO (by 1000 ppm NO + 1% O_2) experiments were conducted after the adsorption of hydrocarbons (2000 ppm propylene 90min., and 5% toluene 10 min in Helium total flow rate 100 cc/min) at 400°C and desorption. The experiments were conducted on Co- and H-ZSM-5 catalysts. The results were calculated and presented as the ratio of NO used for oxidized deposits per oxidized carbon from deposits (the calculation method showed in appendix), as show in table 5.1. As show in table 5.1,

the amounts of carbon deposits on catalyst were depended on type of loaded cation and type of adsorbed hydrocarbon. These results can be implied that the intermediates formation reaction is influenced by both type of loaded cation and type of adsorbed hydrocarbon. This nature corresponding with literature of Chen *et al.*[38], which observed that the deposits are different for n-C₄H₁₀ and i-C₄H₁₀, then it can be suggested that the nature of deposits depend on type of hydrocarbon. The results show in table 5.1 indicated that the NO used for oxidized deposits per oxidized carbon from deposits ratios were nearly close in the case of same catalysts (same loaded cation) although the type of adsorbed hydrocarbons (propylene or toluene) and amounts of carbon deposits on catalyst were different. Considering these ratios of the adsorption of the gas mixtures of C₃H₆+NO+O₂ at 100°C which the deposits formed were contained nitrogen and the adsorption of C₃H₆ or toluene at 400°C which the deposits formed were contain no nitrogen, but these ratios also nearly equal each other in despite of the adsorption temperatures were different. These results can be indicated that the intermediates removal reaction mainly depend on the type of loaded cation on ZSM-5 catalyst but it is less depend on adsorbed gas mixtures (hydrocarbons or hydrocarbon+nitrogen species), adsorption temperature or the type of deposits and amount of deposits.

Considering the ratio of NO used for oxidized deposits per oxidized carbon from deposits comparing between Co-ZSM-5 and H-ZSM-5, the results show that these ratio of H-ZSM-5 are higher than the ratios of Co-ZSM-5. This can imply that H-ZSM-5 is active in NO reduction in the intermediates removal reaction step more than Co-ZSM-5. But Co-ZSM-5 is active in intermediates forming reaction step more than H-ZSM-5 due to the higher amount of formed deposits on Co-ZSM-5. Then, it can conclude that Co-form is active in the first main step involving intermediates formation and H-form is active in the second main step involving intermediates removal. This phenomenon can be the explanation of the Co/H-ZSM-5 nature that the increase of Co content enhances activity of NO conversion up to limit value, excess amount of cobalt appears to suppress activity for NO removal of catalysts [47]. As discuss above that Co cation is more active for intermediates formation and H cation is more active for intermediates removal, then it can be explained that the suppression of NO reduction reaction when cobalt was over loading may be due to the decrease of H cation which active for intermediates removal reaction. And the

optimum cobalt content may be the optimum point between the amount of cobalt cation which active for intermediates formation and the amount of H cation which active for intermediates removal.

catalyst	adsorbed gas/ adsorbed temp/ oxidizing gas	amount of carbon deposits on catalyst	ratio of NO used for oxidized deposits per oxidized carbon from deposits
Co-ZSM-5	C ₃ H ₆ /400°C/NO+O ₂	0.21	0.41
	toluene/400°C/NO+O ₂	0.38	0.35
	C ₃ H ₆ +NO+O ₂ /100°C/O ₂	0.69	-
	C ₃ H ₆ +NO+O ₂ /100°C/ NO+O ₂	0.63	0.40
H-ZSM-5	C ₃ H ₆ /400°C/NO+O ₂	0.12	1.19
	toluene/400°C/NO+O ₂	0.20	1.15

Table 5.1 ratio of NO used for oxidized deposits per oxidized carbon from deposits calculated from TPO results after adsorbed by hydrocarbon and desorption

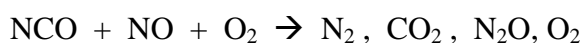
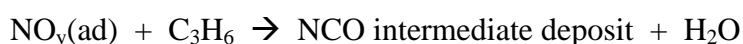
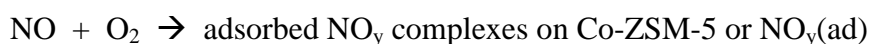
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1) Conclusions

As discussed above chapter, it can be briefly concluded below.

- 1.) Accumulation of deposits, which can not remove at the reaction temperature, can suppress SCR reaction.
- 2.) Type of hydrocarbon employed a reductant affects on formation of intermediates which dominantly play in SCR reaction.
- 3.) Deposits that can remove in oxidizing atmosphere at high temperature are called reversible poison. The conversion is restored when deposit is removed.
- 4.) The presence of oxygen was found to enhance the NO interaction with Co-ZSM-5, leading to the formation of adsorbed NO₂ intermediates [6].
- 5.) Intermediates forming step in SCR reaction mostly occur in the co-interaction of three reactants, C₃H₆, NO, O₂.
- 6.) Intermediate deposits removing reaction is occurred effectively with O₂, and this reaction will occur at lower temperature region in the presence of both NO and O₂. Consequently, the corporation of NO and O₂ can accelerate the intermediate deposits removing reaction.
- 7.) In the removed intermediates reaction, the nitrogen product is produced from nitrogen both in intermediate deposits and in gas phase (from NO). It can imply that intermediate deposits act as reductant for reacting with NO or NO₂ to produce N₂ product.
- 8.) The mechanism scheme of our results attributed to the literatures is proposed as follows:



- 9.) Amount and N/C ratio of deposits increase with adsorbed time.

- 10.) Amount of deposits increases with increasing adsorbed temperature until about 300°C, and then it decreases.
- 11.) N/C ratio decreases with increasing adsorbed temperature.
- 12.) Deposit removal reaction mainly depends on a type of loaded cation on ZSM-5 zeolite more than a type of adsorbed hydrocarbon.

6.2) Recommendations for future studies.

From the previous conclusions, the following recommendations for future studies are proposed.

- 1.) The mechanism should be studied with this technique using other metal loaded ZSM-5 zeolite in SCR reaction.
- 2.) The mechanism should be studied with this technique in SCR for ZSM-5 zeolite with varying hydrocarbon as a reducing agent.
- 3.) To determine the nature of ZSM-5 zeolites in SCR reaction, the specific technique should be improved.



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APPENDIX

SAMPLES OF CALCULATION

1.) Calculation of Reaction flow rate

The catalyst used	=	0.20	g
Packed catalyst into quartz reactor diameter	=	0.6	cm
Determine the average high of catalyst bed	=	X	cm
So that, volume of catalyst bed	=	$\pi * (0.3)^2 * X$	ml
Used GHSV (Gas Hourly Space Velocity)	=	20,000	h ⁻¹
GHSV = $\frac{\text{volumetric flow rate}}{\text{Volume of catalyst}}$	=	20,000	h ⁻¹

$$\text{Volumetric flow rate} = \text{volume flow rate}^t * (273.15/(273.15+t))$$

where t = room temperature, °C

2.) Calculation of gas concentration from area of gas chromatography result.

To convert the area of gas chromatography (GC) to gas concentration, the calibration test was conducted to find calibration equation. The calibration equation was a relation between area from GC and gas concentration. For example:

The calibration of CO ₂ was:	Area	=	1.2608*(concentration(ppm))
If the area of CO ₂		=	100
Then, the CO ₂ concentration		=	$100/1.2608 = 79.3 \text{ ppm}$

3.) Calculation of NO and HC conversion

The effluent gas was analyzed by gas chromatography, the NO reduction activity was evaluated in terms of the conversion of NO into N₂.

$$\text{NO conversion (\%)} = (2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}}) * 100$$

The HC oxidation activity was evaluated in terms of the conversion of HC into CO and CO₂.

$$\text{HC conversion (\%)} = (([\text{HC}]_{\text{in}} - [\text{HC}]_{\text{out}})/[\text{HC}]_{\text{in}}) * 100$$

4.) Calculation of amount of nitrogen and carbon on catalyst

The amounts of nitrogen and carbon on catalyst were calculated from TPO results. The TPO results were the relation between CO₂ or N₂ concentration and temperature or time. The calculation procedure as follows:

- Calculates the total area of the TPO result plots between CO₂ or N₂ concentration (ppm) and time (min):
$$\text{total area} = A \quad (\text{min})$$
- The calculated total area was divided by 1,000,000 and multiply by the total flow rate of gas mixture (0.1 liter/min):
$$B = (A/1,000,000) \cdot (0.1) \quad (\text{liter})$$
- Use ideal gas equation (PV = nRT) to convert gas volume (B) to amount of gas (mole):
$$n = (PV/RT)$$
$$= (1 \text{ atm}) \cdot (B \text{ liter}) / [(0.082) \cdot (303)]$$
- The amount of carbon on catalyst was equal to the amount of calculate CO₂ and the amount of nitrogen on catalyst was equal to the amount of calculate N₂ multiplied by two.

5.) The calculation of N/C ratio of the deposits

This value was derived from the result of temperature programmed oxidation (by 1% O₂) after adsorbed by adsorption gas mixture and desorption. The N/C ratio of the deposits was calculated from the dividing of the amount of nitrogen on catalyst and the amount of carbon on catalyst (The calculation of the amount of nitrogen on catalyst and the amount of carbon on catalyst were show above.).

6.) The calculation of NO used for oxidized deposits per oxidized carbon from deposits

This value was derived from the result of temperature programmed oxidation (by 1000 ppm NO + 1% O₂) after adsorbed by hydrocarbon and desorption.

- The amount of detected N₂ from reactor outlet (mole) was multiplied by 2, then it presented as the amount of NO used for oxidized deposits (mole).

- The amount of detected CO_2 from reactor outlet (mole) was equaled to the the carbon from deposits that had been oxidized by oxidized gas mixture ($\text{NO}+\text{O}_2$) (mole).
- Then, the ratio of NO used for oxidized deposits per oxidized carbon from deposits was the dividing of the two amounts above, respectively.



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