

CHAPTER II

LITERATURE REVIEWS

All the reactions of organic compounds on solid catalysts are accompanied by the formation of heavy by-products, which form a deposit on the surface and provoke deactivation. This chapter present about the studies of the formation and the removal of an intermediate of nitrogen oxide reduction by hydrocarbons on the zeolite catalysts and related subjects that had been studied by many researchers as follows.

2.1 Literature reviews

The catalytic decomposition of nitrous oxide to nitrogen and oxygen was studied over a number of catalysts by Li and Armor (1992). 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) 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 of 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) 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) 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).

Li *et al.* (1993) 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 CH₄ 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 H₂O 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.

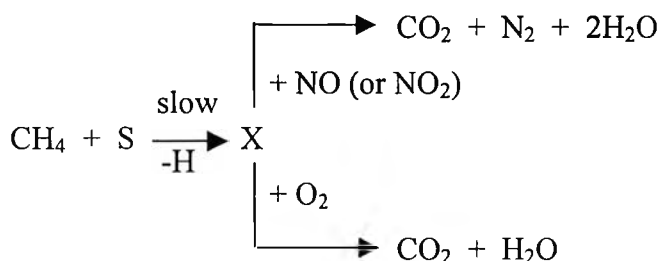
Ansell *et al.* (1993) studied mechanism of the lean NO reaction over Cu/ZSM-5 by used transient techniques. The activation of propene and nitric oxide by Cu/ZSM-5, in the presence and absence of oxygen, have been investigated by temporal analysis of product (TAP) to elucidate the nature of the reducing 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 NO₂-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 -NO₂ species, as the latter approach their limit of thermal stability.

Ditri *et al.* (1993) 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 873 °C. 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

873 °C 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.

Shelef *et al.* (1994) investigated NO₂ formation over Cu-ZSM-5 and the selective catalytic reduction of NO. The extent of the selective catalytic reduction (SCR) of nitric oxide to dinitrogen in the presence of excess oxygen is enhanced by the oxygen on several zeolite-based catalysts and using different reductants. When the catalyst is Cu-ZSM-5 and the reductant is a hydrocarbon, an NO₂ intermediate has been suggested by several investigators. This work shows that at short residence times, with excess reductant and in the absence of oxygen, the NO₂ itself is reduced only back to NO. Thus, for the selective reduction of NO₂ to N₂ (N-pairing) strongly oxidizing conditions are required, same as for the complete reduction of NO. In the presence of excess oxygen the activity of Cu-ZSM-5 in the NO + O₂ reaction to form NO₂ parallels the SCR in every respect. It is higher over Cu-ZSM-5 than on Cu/Al₂O₃ or on H-ZSM-5. The copper-containing zeolite is also active in the decomposition of NO₂ back to NO and O₂ while the other catalysts are much less active. The inhibiting effect of water on the NO + O₂ catalytic reaction is also parallel to the effect on SCR. This evidence strengthens the notion of an NO₂ intermediate.

Cowan *et al.* (1995) 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) evaluated the effect of SO_2 on catalytic performance for the reaction of selective reduction of NO by CH_4 in the presence of O_2 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 H_2O the addition of 53 ppm SO_2 slightly decreased the NO conversion at 500°C but doubled the NO conversion at 550 and 600°C . With the coexistence of 53 ppm SO_2 and 2% H_2O , a substantial decrease in NO conversion was found at $T \leq 550^\circ\text{C}$ but no effect was observed at 600°C . Over a Co-ferrierite catalyst, the addition of 53 ppm SO_2 caused a sharp decrease in NO conversion. With both catalysts, CH_4 conversion was significantly reduced and the CH_4 selectivity greatly enhanced as the result of SO_2 addition. Temperature-programmed desorption measurement of NO adsorbed on fresh and SO_2 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.

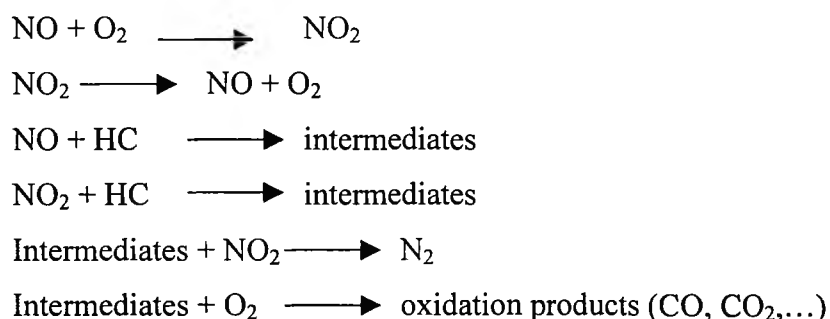
Cant *et al.* (1995) determined the rate-determining step in the selective reduction of nitric oxide by methane over a Co/ZSM-5 catalyst in the presence of oxygen. They studied the relative reaction rate of CH_4 and CD_4 with NO in excess oxygen condition. The rate ratio, CH_4 consumption versus CD_4 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.

Guyon *et al.* (1996) 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. Their 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.



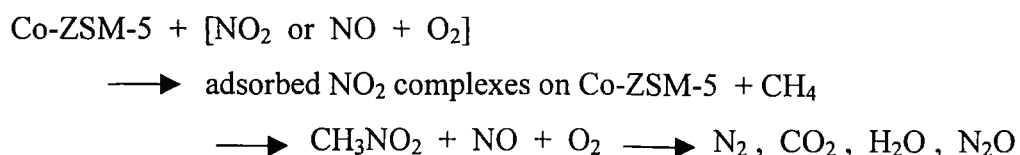
Lukyanov and coworkers (1996) studied the selective catalytic reduction (SCR) of NO with methane over Co/ZSM-5 and H-ZSM-5 zeolites by investigation

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 drawn 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) 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.

Sun *et al.* (1996) 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:

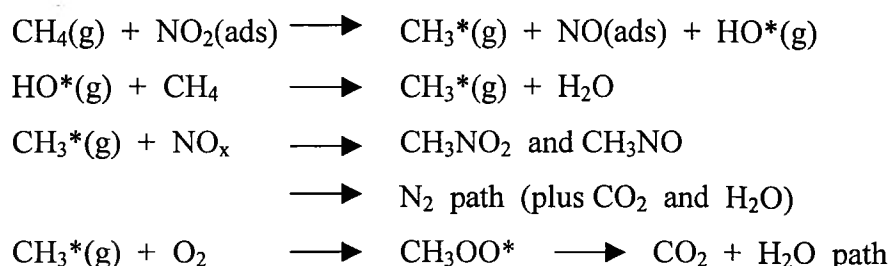


Chen *et al.* (1998) investigated the adsorption complexes of the reduction of NO_x over Fe-ZSM-5. Fe-ZSM-5 prepared via sublimation catalyzes the reduction of NO_x to N₂ in the presence of excess O₂ and H₂O. Propane, isobutane and propene are active reductants; methane is inactive. The NO_x reduction rate is negligible in the absence of O₂; it increases steeply with P-O₂ and passes through a maximum. The equilibrium between NO+O₂ and NO₂ is swiftly established over a clean catalyst, but deposits impede this reaction. NO+O₂ forms chemisorption complexes, NO_y, with y greater than or equal to 2. Upon their reaction with hydrocarbon, a nitrogen-containing deposit is formed on the catalyst. It reacts with NO₂, but not with NO, releasing large

quantities of N_2 . N_2O seems not to be a precursor of N_2 . Isotopic labeling shows that one N atom in every N_2 comes from the deposit; the other comes from NO_2 . Less deposit is formed with propane, more with propene. As deposits also block catalyst sites, the rate limiting step in NO_x reduction depends on the nature of the hydrocarbon. Deposits are oxidized by O_2 and volatilized by H_2O at high temperature; these processes contribute to the relative efficiency of different hydrocarbons in NO_x reduction over Fe-ZSM-5.

de Correa and de P (1998) have studied the reaction of NO_2 , CH_4 and O_2 by using low levels of methane compared to NO_2 and O_2 over protonic and cobalt-exchanged ferrierite, ZSM-5 and mordenite zeolites. Results suggest that two reaction pathways at low and high temperatures may be involved in the lean selective catalytic reduction (SCR) of NO_2 by methane. At low temperatures, the reduction of NO_2 to NO and N_2 might be the initial reaction step. It is likely that NO_2 or its adsorbed precursors initiate the reaction of methane at low temperatures. At high temperatures, the oxidation of NO and combustion of methane with oxygen might be involved. No appreciable differences were observed in the reduction of NO_2 over Co-zeolites as compared to known results of NO reduction over these materials. However, enhanced N_2 formation rate was observed on H-zeolites starting from NO_2 instead of data reported for NO . Furthermore, it appears that the active sites for SCR are both acid and metal sites.

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



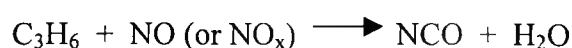
From the literature of Misono (1998), it mentioned the mechanism for NO reduction in the systems NO-C₃H₆-O₂ catalyzed by Ce-ZSM-5. Relative reactivities in the order of NO₂-HC-O₂ ≈ NO₂-HC >> NO-HC-O₂ > NO-HC is one of the experimental facts to support this mechanism. It proposed that selective catalytic reduction by propylene (C₃H₆-SCR) over Ce-ZSM-5 proceeds by the following three-step mechanism.



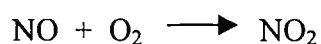
Where X is an organic nitro and/or nitrite compound. The importance of the first step is evident, for example, from the following fact. Na-ZSM-5, which has little activity for the oxidation of NO to NO₂, is not active for NO reduction in a mixture NO-C₃H₆-O₂, but becomes active when NO₂ is used instead of NO, in a NO₂-C₃H₆-O₂ reaction. This also indicates that Ce (or a proton) catalyzes the oxidation of NO. Once NO is oxidized to NO₂ the subsequent reactions with C₃H₆ are rather fast for both Na- and Ce-ZSM-5 catalysts. The reaction between C₃H₆ and NO₂ occurs even on the surface of silica at low temperature, as detected by IR. But the rate of N₂ formation is still slower for Na-ZSM-5 than for Ce-ZSM-5, showing that the NO₂-C₃H₆ reaction to form N₂ is accelerated more by cerium than by sodium or by protons.

Goryashenko *et al.* (1998) studied the mechanism of the selective catalytic reduction of NO with propylene over Co-ZSM-5 by means of in-situ FT-IR. Propylene was activated easily by NO in the absence of oxygen above 200 °C, leading to the formation of three different type of surface NCO species; Co-bonded (2235 and 2195 cm⁻¹), Si-bonded (2300 cm⁻¹ and Al-bonded (2272 cm⁻¹), These surface NCO species were stable in NO or oxygen atmosphere up to 400 °C but in NO+oxygen they were easily converted to the final products of N₂ and CO₂. It is supposed that the SCR of NO_x over Co/ZSM-5 occurs through the Co- and Al-bonded NCO intermediates and its conversion in the rate-limiting step. The 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.



Praserthdam *et al.* (1998) have investigated the comparison of coke deposition on catalysts in reaction with and without oxygen. Two types of catalysts, i.e. Pt/gamma Al₂O₃ and Cu/Na-ZSM-5, were used to investigate the catalyst activity and amount of coke formation on the spent catalysts. The reactions of particular interest were the hydrocarbon oxidation and the SCR of NO with and without O₂. Propane and propene were used as the hydrocarbon sources. The reaction conditions were as follows: reaction temperature = 170-500 °C, GHSV = 4,000 hr⁻¹, TOS = 2 hrs, feed composition depending on each reaction, but the composition of gases were fixed as HC = 3,000 ppm, NO = 1,000 ppm and O₂ = 2.5%, using He balance. It was found that both the case of Pt/gamma Al₂O₃ and the case of Cu/Na-ZSM-5, propene provided higher conversion and coke deposition than propane in the presence or the absence of O₂ and/or NO. For Pt/gamma Al₂O₃ catalyst, in case of the absence of oxygen reactions, the propene conversion dropped more rapidly than the propane conversion. Finally the reaction of propene gave a lower percent of hydrocarbon conversion than the reaction of propane. Additionally, propene had a higher percent selectivity of coke formation for the reaction with the absence of oxygen, but propane had a higher percent selectivity of coke formation for the reaction with the presence of oxygen. For Cu/Na-ZSM-5, in the system with absence and presence of oxygen, the addition of oxygen caused a significant change in % of coke selectivity. With the presence of NO_x, the percent conversion of both propane and propene decreased and that the % coke selectivity of propane decreased, whereas that of in propene increased.

Chen *et al.* (1999) studied the reaction intermediates in the selective catalytic reduction of NO_x over Fe/ZSM-5. For the selective catalytic reduction of NO_x with alkanes to N_2 over Fe/ZSM-5 catalysts, prepared by sublimation, we had previously shown that NO is oxidized over Fe-oxo ions to NO_2 which forms chemisorbed NO_y complexes. Subsequent reaction of the NO_y groups with alkanes results in N-containing deposits that react with different adsorbed NO_2 molecules to form N_2 . At low temperature, the reactivity of n-butane exceeds that of i-butane. Quantitative evaluation of the reaction kinetics for the deposits from not only propane and butanes but also adsorbed model compounds, including ammonia, amines, nitriles, and isocyanates, provide information on the reaction steps on the catalyst surface. Reaction of NO_2 with the catalyst deposit follows Langmuir-Hinshelwood kinetics. The primary intermediates which contain N atoms at a high valence state have to be transformed into deposits containing amino groups. Nitrogen-nitrogen bonds are formed when these groups react with adsorbed NO_2 . The chemical reactions, transforming the primary intermediate into a deposit containing N atoms in a low oxidation state, are easy if an H atom is available in the a position with respect to the NO_2 group; the absence of such H atoms in the primary product from i-butane is the cause for its lower reactivity.

Dossi *et al.* (1999) explored that carbonaceous material entrapped in the channels system of Cu-ZSM-5 catalysts may contribute to maintain the copper ions in the oxidation state +1 by using a multi-technique analytical approach. This suggests that the reduction of Cu^{2+} to Cu^+ does not only occur via water elimination from CuOH^+ species or via oxygen evolution from $[\text{Cu-O-Cu}]^{2+}$ species, but also via oxidation of the carbonaceous materials to give CO and CO_2 . This mechanism occurs under high temperature ($>300\text{ }^\circ\text{C}$) treatments in vacuum or He of Cu-ZSM-5 catalysts containing carbonaceous species and strongly adsorbed water molecules in the first coordination shell of the Cu^{2+} . Our results may support the hypothesis about the roles of O_2 and hydrocarbons in the SCR of NO_x ; O_2 maintains together with hydrocarbons the optimal valence state of copper (Cu^+) necessary to have the maximum conversion of NO_x and hydrocarbons into N_2 and CO_2 .

Lobree *et al.* (1999) studied the interactions of NO, O₂ and NO₂ with Fe/ZSM-5, as well as the reduction of NO by C₃H₈ in the presence of O₂ by using in situ infrared spectroscopy. The sample of Fe-ZSM-5 (Fe/Al=0.56) was prepared by solid-state ion exchange. NO adsorption in the presence of O₂ produced only mono- and dinitrosyl species associated with Fe²⁺ cations. Adsorbed NO₂/NO₃ species are formed via the reaction of adsorbed O₂ with gas phase NO or by the adsorption of gas-phase NO₂. The reduction of NO in the presence of O₂ begins with the reaction of gas phase C₃H₈ with adsorbed NO₂/NO₃ species to form a nitrogen containing polymeric species. A reaction pathway is proposed for the catalyzed reduction of NO by C₃H₈ in the presence of O₂.

Chen *et al.* (2000) investigated the reduction of NO_x over various Fe/zeolite catalysts. A systematic comparison was made of the catalytic activity of a variety of Fe/zeolite catalysts in the selective catalytic reduction of NO_x with isobutane or propane, both with dry and wet feeds. All catalysts were prepared by subliming FeCl₃ vapor onto the H-form of the zeolite, followed by Cl removal. The activities decrease in the order Fe/BEA > Fe/MFI >> Fe/Fer > Fe/MOR approximate to Fe/Y. These differences are rationalized in terms of our mechanistic model and the known pore geometry of the zeolites. FT-IR showed that some Fe loaded narrow pore zeolites are able to oxidize NO to NO₂ and form No_y chemisorption complexes, but unable to let iso-butane enter the pores. Unlike some wider pore zeolites that become covered by a carbonaceous deposit at low temperature, these materials retain their high activity for NO oxidation. Mixtures of Fe loaded wide and narrow pore zeolites, therefore, lead to higher steady-state activities at low temperature than single catalysts. In particular, the combination of Fe/MFI with Fe/FER displays a spectacular activity enhancement.

Panit (2000) investigated the 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 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 roles in selective catalytic reduction of NO with hydrocarbon over Co-ZSM-5 catalyst.

Srihiranpullop (2000) determined the probability of chain growth of coke formation on metals and supported of Pt/ γ -Al₂O₃ by using the Schulz-Flory distribution theory. The main goal of this research was to study the distribution and probability of chain growth of coke on the metal sites and on the support sites. At the beginning, the combination of Pt/SiO₂ representing the metal sites and Al₂O₃ representing the acid sites was investigated. Considering conversion, metal site, H₂ uptake and the nature and amount of coke, interestingly, it was found that Pt/SiO₂ with 100-120 mesh mixed with Al₂O₃ 60-80 mesh has coking behavior similar to Pt/ γ -Al₂O₃. TPO, ESR, IR, BET, XRD, TEM and Soxhelt extraction analyzed with GC-14B were employed for characterization. It was obvious that the effects of time, temperature, H₂/HC ratio and modification of catalysts greatly affected reducing of the amount and probability of chain growth of coke. By considering coke formation on the metal sites and on the support sites, it was found that probabilities of chain growth on both sites were the same. However, the greater accumulation was occurred on the support. This offered the transformation on gas phase of coke intermediates from the metal, which was primarily responsible for producing the coke precursors, to the support as proposed in this model of coke formation. Since coke on the metal had a lower degree of polymerization, the coke was rich in hydrogen.

Teraoka *et al.* (2000) have studied the reaction mechanism of simultaneous catalytic removal of NO_x and diesel soot particulates. Reactions of diesel soot and NO_x with and without O₂ were carried out over CuFe₂O₄ catalyst. The ignition temperature of soot with the NO+O₂ feed was lower than that in O₂ or NO but close to those in NO₂ and NO₂+O₂, indicating the implication of NO₂ especially in decreasing the ignition temperature. On the other hand, the reduction of NO_x into N₂ was enhanced by coexisting O₂. Based on these results and mechanisms of O₂-soot and

NO-soot reactions, the possible reaction mechanism of the simultaneous NO_x -soot removal with the $\text{NO}+\text{O}_2$ feed has been proposed.

2.2 Comment on previous works

There were many literatures that studied the NO reduction with light hydrocarbon such as propane, propene and butane over ZSM-5 catalysts. But there were less literatures that concerned the NO reduction with other hydrocarbons and other zeolite catalysts, then it was interesting to investigate the NO reduction with other hydrocarbon such as toluene (to represent aromatic hydrocarbon) on other zeolite catalysts. On the other hand, for the removal mechanism of the intermediate, there were many researches about the metal oxides catalysts and there were less studies about zeolite catalysts. Therefore, there is an idea to investigate the phenomenon of the formation and the removal of NO_x by propene and toluene on various zeolite catalysts.

In this thesis, the adsorption experiments were conducted to test the mechanism of forming intermediates, and temperature program oxidation were conducted to test the mechanism of removing intermediates converting to the final products. Moreover, the multi methods for the characterization of catalysts are also investigated.