CHAPTER II

LITERATURE REVIEWS

Recently, selective catalytic reduction of nitric oxide with hydrocarbons has received great attention both from an academic and an industrial point of view because this may offer an effective way of removing nitric oxides even in the presence of a large excess of oxygen, whereas present automotive catalysts do not work effectively under this condition. Hydrocarbons as reductants have been extensively studied on several zeolite catalysts. Co/ZSM-5 appears to be the most active zeolite-based system with the presence of methane as reducing agent, but other studies have shown some kinds of metallosilicate and also H-ZSM-5 to be able to catalyse this reaction, but with higher hydrothermal stability or at higher temperatures. The most common studies are as follows:

US. Patent No 5-149-512 [13] 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.

The catalytic decomposition of nitrous oxide to nitrogen and oxygen was studied over a number of catalysts by Li and Armor [14]. 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-erionite, Cu/L, Co/L, Ni/ZSM-5, Mn/ZSM-5) and metal oxide (CuO/Al_2O_3, and CoO/Al_2O_3). For noble metal catalysts, a cation exchanged ZSM-5 has higher activity than the Al_2O_3 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.

Li and Armor [2] 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 [3] further investigated the catalytic reduction of NO_x with methane in an oxidizing atmosphere over many kinds of metal exchanged zeolites and found that the combination of Co^{2+}, Mn^{2+} and Ni^{2+} with certain types of 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 conditions, Cu/ZSM-5, however, is ineffective for the nitric oxide reduction. Co/Y, which has much more Co^{2+}, is much less active compared 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 = 0.06) compared to Co/ZSM-5 (NO/Co > 1.1) and Co-mordenite (NO/Co = 0.8).

The study of metal exchanged ferrierites as catalysts for the selective reduction of NO_x with methane was contributed by Li and Armor [15]. They found that metal ion (Co^{2+}, Mn^{2+} or Ni^{2+}) exchanged ferrierites are very active catalysts for the reduction of NO_x with methane in the presence of excess oxygen. Co-ferrierite yields about twice the nitric oxide conversion compared to Co/ZSM-5 at $T > 500°C$, previously the most active catalyst reported for this reaction, and Co-ferrierite is more selective in the use of methane. The temperature for maximum nitric oxide conversion is a function of zeolite type and the cation exchanged, and this temperature increases in the following order: Co/ZSM-5 < Co-ferrierite < Mn-ferrierite < Ni-ferrierite. The turnover frequency (TOF) normalized by Co^{2+} is a function of Co^{2+} exchange level and increases with the Co^{2+} loading until it reaches an optimum value, whereas the selectivity for methane decreases with increasing Co^{2+}

loading. The presence of water vapor suppresses the activity of Co-ferrierite; however, under wet conditions, its activity is still much higher than Co/ZSM-5 at T > 500 °C.

The simultaneous, catalytic removal of nitrous oxide and nitric oxide in the presence of excess oxygen and methane or propane was also studied by Li and Armor [16] over Co/ZSM-5. Methane is used for the reduction of nitric oxide while the nitrous oxide is able to compete for the metal sites to under go simultaneous decomposition. Interestingly, while NO_x removal by methane do not readily occur without any oxygen, the presence of nitrous oxide actually enhances the conversion of nitric oxide in the absence of oxygen.

Armor et al. [17] 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 $T \leq 450$ °C but has less of an effect at $T \geq 500$ °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.

The catalytic conversion of NO under O_2 excess conditions with the addition of a low concentration of hydrocarbons on metallosilicate was investigated by Inui and coworkers [18]. The stability of the catalyst structure was compared between ion-exchanged ZSM-5 and metal-incorporated silicate having MFI structure (metallosilicate). The advantage of metallosilicate is emphasized. They evaluated the performance of various kinds of metallosilicates for NO conversion and found that metallosilicates such as H-Co-silicate which has a proper acid strength and redox capacity, in other words, a proper activity for hydrocarbon conversion and hydrocarbon combustion, were the best catalysts for the purpose. The reaction characteristics on the metallosilicate catalysts were explained by the microscopic sequential reaction (MSR) mechanism.

Inui et al. [19] examined the NO decomposition in the presence of excess oxygen and a small amount of hydrocarbons on various kinds of MFI-type metallosilicates. In every case the activity was increased at the temperature range where combustion activity was increased. Among the catalysts tested, Co-silicate which had both redox and acidic properties showed the highest performance. Pt modification to the catalyst resulted in both an increase in combustion activity and a NO decomposition activity at lower temperature, especially on Pt-ion-exchanged Co-silicate. Using these bifunctional catalysts and the control of the oxidation state of the surface during the reaction by addition of a suitable hydrocarbon provides a high performance for the NO decomposition reaction in the excess oxygen atmosphere.

Inui and coworkers [20] studied the performance of a protonated Co-contained silicate catalyst for NO reduction in equivalent conditions to diesel engine exhaust, particularly the effects of co-existence of H_2O, CO_2, and SO_2 in the reaction gas on the catalytic reduction over cobalt containing silicate having ZSM-5 (MFI) structure (Co-silicate). Water vapor retarded only the hydrocarbon conversion to CO_2 but no effect was observed on NO conversion. Addition of CO_2 or SO_2 did not affect the reaction. The stability of H-Co-silicate against H_2O, CO_2, and SO_2 was ascribed to the state of metallic active species which were stabilized by incorporation into the high siliceous MFI structure.

Conversion and combustion of a very low concentration of hydrocarbons on various metallosilicates having MFI structure and different acidities were observed by Inui et al. [21] and then compared to conversion of 1000 ppm NO under the same condition of n-octane combustion. Conversion and combustion of hydrocarbons were dominated by the kinds of metallosilicates having different acid strengths and kinds of hydrocarbons. NO conversion was consistently followed hydrocarbon combustion, although at higher temperature only NO conversion decreased. Acidic property of metallosilicates, therefore, gives an indirect effect on NO conversion through hydrocarbon combustion, which affords various hydrocarbon species having different combustibilities.

Witzel and coworkers [22] investigated two catalytic reaction over MFI zeolites: the selective reduction of NO and the combustion of paraffins. Paraffins of increasing complexity were studied as reducing agents in the SCR of NO over a Na-ZSM-5 zeolite containing Co^{2+}, Ni^{2+} or Cu^{2+} base-exchange cations. A correlation was established between the rates of N_2 and CO_2 formation which were independent of the hydrocarbons employed. The data suggest that NO participates selectively in the combustion process and that the two reactions are coupled.

Burch and Scire [23] investigated the selective reduction of nitric oxide by methane or ethane, in the presence and in the absence of a large excess of oxygen on Cu/ZSM-5, Co/ZSM-5, Rh/ZSM-5 and Pt/ZSM-5 catalysts over a wide range of temperatures. They found that the maximum nitric oxide conversion is higher with ethane than with methane and the temperature of this maximum is lower with ethane. In the absence of oxygen the order of activity is Rh/ZSM-5 > Pt/ZSM-5 > Co/ZSM-5 >> Cu/ZSM-5 with the Cu/ZSM-5 being essentially inactive, while in the presence of oxygen the order is: Rh/ZSM-5 > Co/ZSM-5 > Cu/ZSM-5 >> Pt/ZSM-5 when ethane is used as reductant and: Rh/ZSM-5 > Co/ZSM-5 >> Cu/ZSM-5 > Pt/ZSM-5 when methane is used. The effect of the oxygen content was investigated for the Co/ZSM-5 catalyst and found that with a small quantity of oxygen the catalytic activity decreases markedly; with higher oxygen content the activity of the catalyst rises again. It appears that two different reaction schemes may be operative, one in the absence of oxygen the other in the presence of oxygen. It is concluded that neither carbonaceous deposits, nor nitrogen dioxide formation in the gas phase are important in the reaction mechanism on metal-containing zeolites. They proposed that the reaction is essentially a redox process in which decomposition of nitric oxide occurs on reduced metallic or metal ion sites (the relative activity of each of these depending on the choice of metal) leading to the formation of gaseous nitrogen and adsorbed oxygen, followed by the removal of the adsorbed oxygen by the hydrocarbon, thus recreating the active centres.

Armor and Farris [24] reported that cobalt exchanged ZSM-5 has remarkably high hydrothermal stability, especially in comparison to Cu/ZSM-5. Calcination of Co/ZSM-5 in 2% water vapor at 750 °C for a period of 99 h has a modest effect upon its activity for nitrous oxide decomposition. Treatment of Cu/ZSM-5 under the same conditions dramatically reduces the performance of the copper exchanged zeolite.

Li and Armor [25] 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 $T \leq 550$ °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 measurements 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.

Petunchi et al. [26] evaluated the role of gas-phase reactions in the mechanism of the selective reduction of NO over Cu-, Co- and H-mordenite using CH_4, C_2H_4 and CH_3OH. Co- and H-mordenite proved to be active and selective for the three reducing agents, while Cu-mordenite was so only when C_2H_4 and CH_3OH were used. Besides being reduced in the presence of O_2, NO acted as a homogeneous catalyst in the oxidation of CH_4 and C_2H_4. A free-radical mechanism similar to the one occurring in the methane partial oxidation reaction could explain that behavior. Interestingly, on Co-mordenite, the conversion of nitric oxide to nitrogen began to occur at similar temperature for both CH_4 and CH_3OH. For both Co-M and Cu-M the NO to N_2 conversion started after the CH_3OH conversion reached 100%. In the gas-phase reaction no NO conversion was observed when CH_4 or C_2H_4 were used as reducing agents, but a 30% of the nitric oxide conversion was obtained when CH_3OH was the reducing reactant at 600 °C. Very similar results were observed with or without O_2 in the feed stream. When catalysts were present, the presence of oxygen noticeably increased the rate of NO to N_2 conversion

Cant et al. [27] 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 reaction 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 reaction 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.

Comparison of catalyzed and homogeneous reaction of hydrocarbon for selective catalytic reduction (SCR) of NO_x was studied by Hall et al.[28]. They reported that when NO_2 (0.21 % in He) was passed over Co/ZSM-5 or H-ZSM-5 at SVH = 45,000 h^{-1}, equilibrium with NO + O_2 was approached at temperatures above 400 °C. They performed the comparison of the reaction of NO_2 + CH_4, NO_2 + CH_4 + O_2, and NO + CH_4 + O_2 over those catalysts with that in the empty reactor. The latter two reactions yielded essentially identical results when catalyzed, as did NO_2 + CH_4 up to about 22 % conversion of CH_4, i.e., to the point where the oxygen supply became exhausted. Without added O_2, NO appeared as a reduction product of NO_2 along with N_2. In the empty reactor, no N_2 was formed although NO_2 could be quantitatively reduced to NO; combustion of CH_4 with O_2 (or with NO) alone was not observed at temperature less than 600 °C, but light-off with NO_2 or $NO_x + O_2$ occurred at about 450 °C. In the absence of O_2, the homogeneous methane conversion was limited to about 22 % at 600 °C where the conversion of NO_2 to NO reached 100 %. With added O_2, conversion of CH_4 reached 62 % at 600 °C and approached 100 % under more severe conditions. These data illustrate the key role played by NO_2 in the selective catalytic reduction reaction. They also show that a catalyst is necessary for formation of N_2 and emphasize the importance of O_2 in maintaining an adequate supply of NO_2, particularly at temperature above 527 °C where equilibrium favors NO. When C_3H_8 or i-C_4H_{10} was substituted for CH_4, the order of reactivity was i-$C_4H_{10} > C_3H_8 > CH_4$ in both the catalyzed and the homogeneous reactions. Moreover, in the empty reactor dehydrogenation to the corresponding olefins was found to be important with the former two; the mass balance did not close with CH_4, possibly due to formation of formaldehyde.

Comparative kinetic and in-situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFT) studies of the N_2O decomposition on Co-, Fe- and Cu/ZSM-5 have been performed by Kapteijn et al. [29] so as to evaluate the implications of the presence of O_2, CO, NO, H_2O and SO_2 on the catalyst activity and stability and on the mechanism. The presence of O_2 hardly affects the reaction over Fe- and Co/ZSM-5, but it inhibits slightly for the Cu system due to the molecular or dissociative adsorption of oxygen, although this effect seems to level off at higher oxygen concentrations. In the presence of NO the reaction is enhanced for Fe, and not affected for Co and Cu. Addition of CO also enhances the N_2O conversion, by about a factor of two for Co and tremendously for Fe. For Cu a maximum in the N_2O

conversion appears as a function of the CO/N_2O ratio in the feed. CO addition fastens the removal of surface oxygen and then the active sites are virtually in the reduced form. The kinetic and IR results with NO indicate that, like CO, it can remove the oxygen from the surface of the Co and Fe catalysts, too, thereby forming NO_2. Water exerts both a deactivating and inhibiting influence on Cu and Fe samples, while the reaction over Co is only inhibited. The deactivation of Fe- and Cu/ZSM-5 is clearly due to migration and the sintering of the active component in H_2O atmospheres. SO_2 nearly completely deactivated the Cu/ZSM-5, resulted in an inhibition for Co/ZSM-5 and an enlargement of the N_2O conversion over Fe/ZSM-5.

Hall et al. [30] clarified the role of free radicals NO_2 and O_2 in the selective catalytic reduction (SCR) of NO_x with CH_4 over Co/ZSM-5 and H-ZSM-5 zeolites. They got the results from the reaction of CH_4 with the mixture of NO + O_2 and NO_2 + O_2 and with three oxidizing components separately and determined the differential reaction rate. Comparison of the light-off temperature as well as the activation energies of these reaction led to the conclusion that the SCR of NO_x into N_2 and, consequently, CH_4 oxidation into CO_x are initiated by the reaction of CH_4 with NO_2. At low temperature (300-400 °C) O_2 does not compete with NO_x for CH_4, and its role is limited to the oxidation of NO into NO_2. However, at higher temperatures a strong competition between NO_x and O_2 for CH_4 results in a decrease in the selective of the SCR process. It is shown that this competition is stronger with Co/ZSM-5 catalyst than with H-ZSM-5, and this explains the higher selectivity observed with the latter catalyst. Based on these observations the formation of the $CH_3\bullet$ free radical is postulated and lead to the possible pathways of the SCR of NO_x into N_2.

An in situ infrared investigation of the reduction of NO by CH_4 on Co/ZSM-5 was conducted by Aylor and coworkers [31]. In the presence of O_2, NO_2 is formed via the oxidation of NO. Adsorbed NO_2 then reacts with CH_4. Nitrile species are observed and found to react very rapidly with NO_2, and at a somewhat slower rate with NO and O_2. The dynamics of the disappearance of CN species suggests that they are reactive intermediates, and that N_2 and CO_2 are produced by the reaction of CN species with NO_2. 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 to explain the role of O_2 in facilitating the reduction of NO by CH_4, and the role of NO in facilitating the oxidation of CH_4 by O_2

The abatement of NO with CH_4 in the presence of oxygen ([NO] = [CH_4] = 1000 or 4000 ppm, [O_2] = 0 to 2%, by volume) was studied by Campa et al. [32] on Co/ZSM-5 catalysts (Co content 0.29 to 4.1 wt.%), prepared from H-ZSM-5 or Na-ZSM-5 by the ion-exchange method. On all samples, the amount of CO and NO adsorbed at room temperature was proportional to the cobalt content (CO/Co ≈ 0.5 and NO/Co ≈ 1.6), with the exception of the Co/ZSM-5 sample with Co 4.1 wt.%, on which the adsorption was only slightly higher than that on Co/ZSM-5 with Co 2.0 wt.%. Infrared spectroscopy (FTIR) showed the formation of carbonyls (one type only, on cobalt equivalent sites), cobalt mononitrosyls (two types) and dinitrosyls (two types). The intensity of bands from carbonyls and nitrosyls was about proportional to the cobalt content, with the exception of the Co/ZSM-5 sample with Co 4.1 wt.%, on which the band were roughly as intense as in the sample with Co 2.0 wt.%. In the Co/ZSM-5 sample with Co 4.1 wt.%, after heating with O_2 at 500 °C, or after its use in catalysis, diffuse reflectance spectroscopy (DRS) showed the presence of Co_3O_4, not detected by X-ray diffraction. In the presence of O_2, the NO reduction rate was proportional to the Co content, except for the sample containing Co 4.1 wt.%. The CH_4 oxidation rate was proportional to the Co content, in the entire range of Co concentrations. The selectivity of catalysts for NO abatement (selective catalytic reduction, SCR), was nearly independent of Co content but was markedly lower on the sample with Co 4.1 wt.%. The results suggest that only Co^{II} ions exchanged in the framework of the ZSM-5 matrix are active in CO and NO adsorption and in the SCR reaction, whereas also the cobalt of the dispersed Co_3O_4 phase contributes to CH_4 oxidation with O_2.

Stakheev et al. [33] studied the selective catalytic reduction (SCR) of nitric oxide (NO) with propane over Co/ZSM-5 catalysts with a series of exchanged cobalt concentrations (0.9-7.5 wt.%). The overall activity for SCR of NO is found to increase linearly with the cobalt content in the range below the maximum exchange capacity (Co/Al = 0.5). However, when the cobalt loading exceeds the exchange capacity of the zeolite, viz. Co/Al > 0.5, the combustion of propane is favored significantly, resulting in a decrease of the NO conversion. The presence of excess Co^{2+} in zeolite appears to bring about the marked falls in adsorption of NO. In this case cobalt oxide particles are presumed to form, which promote the oxidation of propane. Nevertheless, the addition of alkaline-earth metal cations (Ba, Ca) resulted in the suppression of propane oxidation over Co/ZSM-5, and improved the NO conversion dramatically.

The study of mechanistic cause of hydrocarbon specificity over Cu/ZSM-5 and Co/ZSM-5 catalysts in the selective catalytic reduction of NO_x was conducted by Sachtler et al. [34]. They identified the nature of adsorbed nitrogen oxide complexes (NO_y) by FTIR spectroscopy. Nitrito groups are most prominent on Co/ZSM-5. These complexes are stable at 150°C in He but are reduced upon exposure to either C_3H_8 or CH_4 leading to the formation of N_2. Conversely, Cu/ZSM-5 forms nitro and nitrate groups which are stable at 200°C. At this temperature these complexes are chemically reduced to N_2 upon exposure to C_3H_8 yet remain inert to CH_4. At higher temperature, thermal decomposition yields NO/NO_2, O_2, and H_2O. The specific rate of NO reduction over Cu/ZSM-5 decreases with Cu loading indicating that isolated $Cu^{2+} \cdot NO_2$ complexes pay a significant role in the mechanism. The hydrocarbon specificity of these complexes thus matches the known catalytic specificity of NO_x reduction over Cu/ZSM-5 and Co/ZSM-5. The mechanistic cause for the catalytic specificity of the ZSM-5 hosted metals in NO_x reduction thus is traced back to the structure and reactivity of the specific NO_y adsorption complexes which these metals produce upon interacting with NO + O_2. The consumption of CH_4 when feeds containing NO, CH_4, and O_2 are exposed to Cu/ZSM-5 can be attributed to nonselective combustion with adsorbed oxygen and not to reactions with NO_y.

Halasz et al. [35] studied the catalytic activity and selectivity of H-ZSM-5 for the reduction of nitric oxide by propane in the presence of oxygen at various conditions. The reaction can result in the formation of either NO_2 or N_2. The selectivity for N_2 mainly depends on the ratio of NO/C_3H_8 in the feedstock; the reaction temperature and the concentration of O_2 have only minor influence. When the concentration of NO is 1000 ppm (which is typical for automotive exhausts) and $NO/C_3H_8 > 1$, the oxidation of NO to NO_2 dominates, but the NO_2 does not react significantly with C_3H_8 at these reaction conditions. NO can be reduced by C_3H_8 selectively to N_2 at $NO/C_3H_8 \leq 1$ when oxygen is present. Results suggest that the selective catalytic reduction (SCR) of NO can proceed via two different reaction pathways below and above 500 °C. At low temperature, the oxidation of NO by O_2 to NO_2 might be the initial reaction step. Below 500 °C, this reaction is much faster than other possible reaction in the mono- or bimolecular mixtures of the three reactants. At 500 °C, the reaction rate of the oxidation of C_3H_8 by O_2 is comparable to that of the NO oxidation. At 600 °C, the oxidation of C_3H_8 is faster than other reaction in the mono- or bimolecular mixtures of reactants. Thus, probably the combustion of propane initiates the SCR process above 500 °C. The rate of both initial reactions depend on the concentration of oxygen and the reaction temperatures, but contrary to common belief that these parameters have little effect on the yield of N_2 in the SCR process. It appears that the active sites for the reaction of $NO + O_2$, $C_3H_8 + O_2$, and $C_3H_8 + NO_2$ are similar to each other, probably involving the Brønsted acidic bridging hydroxyls of H-ZSM-5. When $NO/C_3H_8 > 1$, adsorbed NO_x species may prevent the adsorption of C_3H_8 since propane barely reacts with the other reactants. At $NO/C_3H_8 \leq 1$, the SCR of NO to N_2 probably proceeds via the secondary reactions of $C_3H_8 + NO_2$ (below 500 °C) or $C_xH_yO_z + NO_x$ (above 500 °C). Radicals are likely involved in both the initial and the secondary reaction steps. At 300 °C, the probable overall stoichiometry of the SCR process is $2C_3H_8 + 6NO + 4O_2$

$\rightarrow 6CO + 8H_2O + 3N_2$. At higher temperatures, CO_2 also appears in the products and the efficiency of propane to form N_2 decreases.

Lukyanov and coworkers [36] 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 the reaction of CH_4 with NO, NO_2, and O_2, and with the mixtures of $NO_x + O_2$. 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 N_2 and CH_4 oxidation into CO_x are coupled and initiated by the reaction of CH_4 with NO_2. The results demonstrate that this reaction may be considered as a limiting reaction step of NO_2 reduction into N_2, and of the SCR reaction for the mixture of $CH_4 + NO + O_2$ when O_2 is present in large amounts. With the latter mixture when O_2 concentration is relatively low (up to about 1.5 %) another reaction step, namely, the catalytic oxidation of NO by O_2 into NO_2 appears to control the rate of the SCR process. Thus, an important role of O_2 is to convert NO into NO_2. At low temperature (below 400 °C) O_2 does not compete with NO_x for CH_4, but even at these temperatures O_2 participates 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 O_2 and NO_x for CH_4 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 O_2 and NO_2 for CH_4 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 $CH_3\bullet$ free radical and possible reaction of this radical with NO_x and O_2, that form the pathways of the SCR process, are postulated. Also, the possible role of gas phase reactions in the SCR process is considered.

The decomposition of nitrous oxide on several Co- and Cu/ZSM-5 zeolite catalysts was studied by Correa et al. [37] in the absence and presence of excess oxygen. They also evaluated the effect of methane addition, as well as catalyst steaming in dry and wet feeds. N_2O decomposition with no oxygen in the feed was proportional to metal loading on both catalysts. Co/ZSM-5 was much more resistant than Cu/ZSM-5 in excess oxygen. The tolerance of Co/ZSM-5 catalysts to excessive amounts of oxygen is high when Co^{2+} is stabilized in the zeolite framework and depends on the catalyst method of preparation. The presence of methane with no oxygen in the feed enhanced N_2O decomposition while the addition of both methane and oxygen to the feed decreased N_2O conversion on all catalysts tested. Co^{2+} ions stabilized by ZSM-5 framework have high hydrothermal stability in comparison to Cu^{2+}-exchanged ZSM-5.

Stakheev et al. [38] studied the formation of NO_2 and its effect on the selective catalytic reduction of NO over Co/ZSM-5. They compared the catalytic performance of Co/ZSM-5 with different metal loading and of H-ZSM-5 in the $NO + O_2$, $C_3H_8 + O_2$, and $NO + C_3H_8 + O_2$ reactions and found that Co/ZSM-5 catalysts containing only isolated cobalt ions in cationic positions are inactive in NO_2

formation. To achieve appreciable NO conversion in the SCR process over these catalysts, higher reaction temperatures are required. These results make it possible to suggest that NO_2 formation is not a prerequisite for the SCR of NO with hydrocarbons over Co/ZSM-5. With increasing Co loading, however, Co/ZSM-5 begins to exhibit activity in NO_2 formation. This is explained by the formation of cobalt oxide particles on the zeolite carrier, which are active in the NO_2 formation. Increase in NO_2 formation strongly enhances catalytic activity in SCR of NO at lower reaction temperature. Comparison of the C_3H_8 conversion in the $C_3H_8 + O_2$ and $C_3H_8 + O_2 + NO$ reactions provides evidence that NO_2 activates hydrocarbon molecules resulting in the formation of the reaction intermediates of the SCR process.

Jentys et al. [39] investigated the structure and stability of $(CoO)_x$ clusters in siliceous ZSM-5 (silicalite) and on SiO_2 using atomistic simulation techniques. The deconvolution of the energy into distortion and interaction contributions revealed that the improved stability of the supported clusters is due to the energy gained from the cluster-host interaction. $(CoO)_x$ clusters in ZSM-5 of between 4 and 6 Co atoms showed an enhanced stability, while cluster larger than 18 Co atoms were sterically limited inside the zeolite lattice.

The effect of water on selective catalytic reduction of NO_x using hydrocarbons (HC-SCR) for natural gas engines over Cu- and Co/ZSM-5 was investigated by Tabata et al. [40]. Co/ZSM-5 showed a higher HC-SCR activity and selectivity using C_3H_8 than Cu/ZSM-5 at temperatures above 400 °C in the presence of water. On Co/ZSM-5, C_3H_8 oxidation by O_2 was slow and severely inhibited by water due to

Co/ZSM-5's poor ability to adsorb O_2 dissociatively, and the capacity for NO adsorption was large enough to supplement the poor NO oxidation activity. These adsorption properties are therefore considered to contribute to the high activity and selectivity observed on Co/ZSM-5.

Inui et al. [41] evaluated the synthesis and catalytic performance of cobalt-incorporated MFI-type silicates. They synthesized MFI-type silicates incorporated with various contents of cobalt ions by the rapid crystallization method. X-ray diffraction analysis, atomic absorption spectrophotometry, UV spectroscopy, ^{29}Si MAS NMR spectroscopy, and X-ray photoelectron spectroscopy were used to investigate the contents and state of cobalt ions. Although the intrazeolitic cobalt ions tended to migrate to the external surface during the calcination and to be removed by washing with water during the ion exchange treatment, cobalt ions could be incorporated stably into the zeolite framework until a Co/(Si+Co) atomic ratio of about 0.0025. Even at a Co/(Si+Co) atomic ratio of above 0.0025, a considerable amount of cobalt ions could be highly dispersed in the internal domain of the zeolite pore matrix.

Jentys et al. [42] characterized the metallic species on Ni- and Co-containing ZSM-5 catalysts. They prepared a series of Co- and Ni-containing ZSM-5 zeolites with varying metal loading by solid-state ion exchange and by wet impregnation. Solid-state ion exchange led to highly dispersed metal ions inside the channels of ZSM-5. For the impregnated samples metal oxide clusters, mainly located on the exterior of the crystallites, were observed. Reduction at 300 °C of Ni/ZSM-5 prepared by solid-state ion exchange led to the formation of small metallic clusters inside the pores, whereas reduction at 500 °C led to the formation of large Ni clusters outside the channels. Co/ZSM-5 could be only reduced at 500 °C, where larger particles were rapidly formed.

Woolery et al. [43] evaluated the nature of framework Bronsted and Lewis acid sites in ZSM-5. They characterized the acidity of aluminum in a nominally 70:1 SiO_2/Al_2O_3 ratio ZSM-5 prepared by conventional means by TPAD, ^{27}Al and ^{29}Si NMR, XRD, and FTIR and found that discrepancies observed between the amount of tetrahedral "acidic" aluminum measured by TPAD and IR versus Al-NMR are due to the presence of Lewis aluminum. Furthermore, it is suggested that this Lewis aluminum may be located in the zeolite framework. These sites are not thought to be inherent to the ZSM-5 structure but are probably generated during calcination, resulting in partial hydrolysis of Al–O bonds. A small percentage of octahedral aluminum was observed in hydrated H-ZSM-5, but was quantitatively converted to tetrahedral aluminum by treatment with ammonium nitrate solution at pH 8.

Satsuma et al. [44] investigated the selective reduction of NO with CH_4 in the presence of excess O_2 over H-ZSM-5 and H-mordenites in the attention to the factors controlling catalytic activity. The activity for the reduction of NO into N_2 was independent of crystal size and pellet size, indicating that the diffusion in zeolite channel and macro-pore has negligible effect on the catalytic activity. The catalytic activity proportionally increased with the acid amount, which strongly indicates that the acid amount is the controlling factor for this reaction. The activity was also dependent on the type of zeolites, which may be due to the difference in the acid strength, but not in the pore structure.

The effects of hydrothermal treatment on the performance of Cu, Co, and Mn exchanged MFI zeolite catalysts for the selective reduction of NO with hydrocarbons has been investigated by Budi and coworkers [45]. It is shown that the deterioration of catalyst activity on exposure to steam is due to dealumination of the zeolite framework, causing loss of cation exchange capacity and residual Br□nsted acidity, and in the case of Cu resultant aggregation of the transition metal component on the external surface of the zeolite.

Stakheev et al. [46] studied the roles of oxygen in selective catalytic reduction of nitric oxide with propane over Co/ZSM-5 catalysts with different cobalt loadings. The catalytic activities in the $NO + C_3H_8 + O_2$, $NO + O_2$, and $C_3H_8 + O_2$ reactions were compared in conjunction with catalyst characterization by TPD of NO and TPR. The data obtained reveals multiple roles of oxygen that depend on the structure of the catalyst. It was found that for the catalysts containing cobalt oxide species NO_2 formation plays important role in the SCR of NO. The catalysts that contain only isolated Co^{2+} ions were found to be inactive in NO_2 formation. Nevertheless, these catalysts also exhibit relatively high NO_x conversion albeit at higher temperature, and their SCR activity was found to be strongly promoted by oxygen. TPD of NO adsorbed on the catalyst precovered with oxygen indicates that oxygen preadsorption decreases the strength of NO adsorption, thus improving the activity.

Inui et al. [47] compared the thermal stability and catalytic performance of deNO_x activity over various MFI-type metallosilicates under the condition of the excess oxygen with a low concentration of hydrocarbon to that over metal ion-exchange ZSM-5 catalysts. The structural changes measured by XRD, BET surface area, and XPS and the decrease in NO removal activity after high temperature calcination were much smaller in the cases of metallosilicates than those of ion-exchanged zeolites. The results conclusively demonstrate a higher potential of metallosilicates for practical application to the purification of exhaust gases coming from lean burn engines and facilities.

Chang and McCarty [48] investigated the decomposition of NO_x over Cu^{2+}- and Co^{2+}-exchanged ZSM-5 zeolites by using isotope labeled $^{15}N^{18}O$ and temperature-programmed desorption (TPD) technique. They found that formation of NO_2 intermediates is responsible for enhancing the rate of NO_x decomposition when the catalyst were treated in both $^{15}N^{18}O$ and O_2. Co-adsorption of $^{15}N^{18}O$ and O_2 led to a dramatic increase in the amount of NO_x and O_2 adsorbed. The surface NO_x species decomposed or desorbed to form NO, O_2, N_2, and NO_2 during the TPD. This results in formation of equal amounts of $^{15}N^{16}O$ and $^{15}N^{18}O$ in NO products and 50% $^{15}N^{16}O^{18}O$, 25% $^{15}N^{16}O_2$, and 25% $^{15}N^{18}O_2$ in NO_2 products. In the absence of O_2, formation of N_2O was observed at < 300 °C but not NO_2. For Cu/NaZSM-5, its N_2O products are exclusively $^{15}N_2{}^{18}O$, suggesting that lattice oxygen is not involved in the formation of N_2O (it is derived solely from was observed at $^{15}N^{18}O$) and the isotope exchange between $^{15}N_2{}^{18}O$ with the zeolite lattice oxygen (^{16}O) is not significant. However, for Co/ZSM-5, formation of either N_2O or NO_2 is negligible with $^{15}N^{18}O$

treatment. Treatment in both $^{15}N^{18}O$ and O_2 resulted in some formation of N_2O, consisting of equal amounts of $^{15}N_2{}^{16}O$ and $^{15}N_2{}^{18}O$, suggesting either isotopic exchange occurred between N_2O and lattice oxygen, or between NO and lattice oxygen, or formation of N_2O involved lattice oxygen. Except that the low-temperature activity for N_2 formation for Cu/NaZSM-5 treated in $^{15}N^{18}O$ alone is due to formation of NO_2 intermediates. The main difference between Cu/Na-ZSM-5 and Co/Na-ZSM-5 is that for Cu/Na-ZSM-5, in addition to the low-temperature activity shared by Co/Na-ZSM-5, it showed significant activity for nitric oxide decomposition at high temperature (>360 °C) while Co/NaZSM-5 showed little. A TOF of $2.88 \times 10^{-4}\ s^{-1} \cdot Cu^{-1}$ for Cu/Na-ZSM-5 at 122 °C and at 0.1 vol.% $^{15}N^{18}O$ and 0.4 vol.% O_2 is even higher than $\sim 2 \times 10^{-4}\ s^{-1} \cdot Cu^{-1}$ report in the literature at >350 °C, but at a much lower temperature. In terms of N_2 formation, Co/Na-ZSM-5 is about 2-3 times more active than Cu/Na-ZSM-5 at low temperature (<200 °C). For Cu/Na-ZSM-5, its activity for NO_2 decomposition is approximately 4 times higher than that for NO at 320-370 °C. Co/Na-ZSM-5 does not show any significant activity for NO decomposition but its activity for NO_2 decomposition is comparable to that of Cu/Na-ZSM-5.

Lobree et al. [49] studied the role of cyanide species in the reduction of NO by CH_4 over Co/ZSM-5. They used in situ infrared for observation the reaction and the presence of CN species was reveals. The reactivity of these species was probed by exposing them to NO_2, O_2, or NO while monitoring their rate of disappearance. In a complementary set of experiments, mass spectrometry was used to identify the reaction products as N_2 and CO_2. At 450 °C the rate coefficients for the consumption of CN are 8.5×10^{-5}, 1.9×10^{-6}, and 3.3×10^{-7} s^{-1} ppm^{-1} for reaction in NO_2, O_2, and NO, respectively. The reactivity of CN is sufficiently high for these species to be considered reaction intermediates in the formation of N_2 and CO_2 during the reduction of NO by CH_4 in the presence of O_2.

The mechanistic study of NO reduction with methane over CO^{2+} modified ZSM-5 catalysts has been studied in an oxidizing atmosphere by Yim et al. [50]. 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 Co^{2+} cations in ZSM-5. The adsorption of NO, NO_2 and CH_4, as well as the reduction of NO with methane in O_2 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 NO_2 intermediates. The adsorbed NO_2 would activate methane molecules and yield hydrogen and methyl radicals, which could in turn react with NO_2 to generate nitromethane intermediates. They proposed the tentative reaction mechanism to elucidate the production of N_2, N_2O, H_2O, formaldehyde and CO_2.

Inui et al. [51] studied the catalytic elimination of NO under the condition of a large excess of oxygen using MFI-type metallosilicates catalysts. In order to realize an on-site supply of active reductants, such as hydrogen and carbon monoxide, steam-reforming reaction of a hydrocarbon, *n*-octane, was investigated in conditions both with and without H_2O. With the addition of H_2O, significant amount of H_2 and CO were recognized in the products, indicating that the steam-reforming reaction occurred even in the presence of a large excess of oxygen. Thus, in situ formed reductants were effectively consumed for NO removal, and consequently resulted in an increase in NO conversion. Such an increase in NO conversion in the presence of H_2O has scarcely been known and this kind of desirable effect would be suitable for the practical reaction gas condition of automobile exhaust.

Inui and coworkers [52] revealed the advantageous features of metallosilicates as the catalysts for elimination of NO in the exhaust gases containing a large excess of O_2 and H_2O. They examined the effect of high temperature calcination in air with and without steam over metal ion-exchanged H-ZSM-5 (Me/H-ZSM-5) and metallosilicates having MFI structure on the BET-surface area and NO conversion. Metallosilicates were much more stable than Me/H-ZSM-5 in both BET-surface area and catalytic performance of NO conversion in the presence of excess O_2 and a low concentration of hydrocarbon. Furthermore, in case of H-Co-silicate, catalytic properties of both hydrocarbon combustion and NO conversion were significantly increased by a high temperature calcination in air stream including steam. The reason is that Co incorporated in the framework was partly but uniformly educed by the calcination, especially with co-existence of steam, and exhibited higher catalytic activity.

The effect of high-temperature steam treatment on the activity of Co/ZSM-5 catalysts for the selective catalytic reduction of NO with methane have been examined by Howe and Budi [53]. They reported that loss of activity and selectivity on steam treatment is due to framework dealumination of the zeolite, causing an irreversible change in the coordination state of the Co^{2+} ions. Pre-exchange of the zeolite with La^{3+} cations inhibits the dealumination while stabilizing the catalysts.

Miller et al. [54] determined the role of the acidic support in ion-exchanged cobalt-zeolite, lean NO_x catalysts by studying the individual steps in the selective reduction pathway. At a GHSV of 10,000 and reaction temperature below 400 °C, NO oxidation is not sufficiently rapid to obtain equilibrium over catalysts. The NO oxidation rate increases in the order $H^+ < Co^{2+} <$ Co-oxide, and neither the number, nor the strength of the acid sites affects the specific rate of the Co^{2+} ions. For reduction of NO_2 by propylene at 300 °C and methane at 400 °C, the formation of N_2 is suggested to occur at support protons sites. In addition, the rate of N_2 formation increases linearly with an increase in the number of acid sites, and the specific activity increases with an increase in acid strength. Cobalt (2+) ions do not contribute significantly to the formation of N_2, but do non-selectively reduce NO_2 to NO. It is proposed that the formation of N_2 occurs by protonation of the reducing agent followed by attack of the carbocation by gas phase NO_2. Thus, the selective reduction of NO requires two catalytic functions, metal and acid sites.

Inui and coworkers [55] reported that enhancement of NO elimination activity over Co-silicate catalyst could be achieved by high temperature calcination. H-Co-silicate, having MFI structure, calcined in steam-containing air at 800 °C was characterized by XRD and diffuse reflectance electron absorption. A part of Co ions incorporated into the framework of H-Co-silicate was educed by calcination and remained nearby with a state of small cluster. The catalytic performance for NO elimination in the presence of excess oxygen on Co-impregnated silicate having MFI structure, H-Co-silicate and a physical mixture of the both catalysts were examined as reference catalysts compared to Co-impregnated H-Co-silicate. The presence of the educed Co ions enhanced the catalytic activity for NO elimination due to the uniform and isolated dispersion of oxidized Co clusters.

Broadening the effective temperature range (window) of NO removal on Co,Pd-modified H-ZSM-5 (Co/Pd/H-ZSM-5) in the presence of methane under an excess oxygen condition was tried by Inui and coworker [56] under the concept that the lack of the amount of methane occurred by CH_4 combustion at high temperature reduced NO conversion to N_2. The activity for NO removal of the catalyst at high temperature was improved due to suppression of methane combustion by the thermal treatment of Pd in a H_2-containing flow. Co/Pd/H-ZSM-5s with and without the thermal treatment of Pd showed different temperature windows for NO elimination. These different windows were then combined by a two-stage catalyst packing, in which Co/(Pd/H-ZSM-5)$_{red.}$ and Co/Pd/H-ZSM-5 were placed in series, resulting in the broadening of the window.

The reaction of nitromethane with NO_2 or NO in the presence of excess O_2 and CH_4 have been studied by Lombardo et al. [57] and the results compared over four catalysts: Co-, H-, Fe-, and Cu/ZSM-5. Data were collected at a series of temperatures for the selective catalytic reduction of NO with CH_4 (SCR) for the former two catalysts for comparison. Product composition data were obtained both chromatographically and by IR analysis of the exit gases. The data showed that, whereas the light-off temperature lower when CH_3NO_2 was substituted for CH_4, they passed through peak conversion to N_2 at the same temperature and then fell off rapidly at higher temperature in the way typical for SCR reactions. The reaction of CH_3NO_2 with O_2 alone produced results similar to those for the SCR reaction, but with roughly 50% of the peak conversion to N_2. The activity of Cu/ZSM-5 in these reaction was much greater than for the other three catalysts. The IR data showed the presence of HCN, NH_3, and HNCO in various low concentration below 400 °C. The concentration of N_2 and N_2O were obtained by GC. These data differed over the four catalysts. All of these compounds have been suggested in the literature as possible intermediates in the formation of N_2 and their behavior in these experiments was not inconsistent with these ideas. These results suggested, however, that one single pathway to N_2 formation does not exist; several optional mechanisms may function as suggested by the earlier literature. When $^{15}N^{18}O+O_2$ was substituted for the unlabeled molecule, the predominant N_2 product was $^{15}N^{14}N$, suggesting that one N-atom is supplied by each of the two reacting molecules, CH_3NO_2 and NO_2.

The reaction of nitromethane over Co/ZSM-5 was studied by Cant et al. [58] with the aim of establishing the paths by which it can be converted to N_2 under the conditions of the methane-SCR reaction over this type of catalyst. When reacted alone it readily decomposes above 250 °C to give CO_2 and NH_3 but the latter is further converted to N_2 at temperatures above 360 °C if NO and O_2 are also present. The reaction of ammonia with NO and O_2 is sufficiently fast to account for all N_2

formed. The nitromethane reaction systems are stable above 300 °C but below that deactivation sets in after a few hours with isocyanic acid (HNCO) eventually becoming the major nitrogen-containing product. If water is then added to the feed the HNCO is largely hydrolysed to NH_3 and CO_2 and conversion stabilises. Reaction in the presence of water at higher temperature restores the original activity. It is believed that HNCO is the initial decomposition product of nitromethane and deactivation under dry conditions is due to its deposition, possibly as a polymer such as cyanuric acid. Nitromethane also decomposes to CO_2 and NH_3 over alumina, H-ZSM-5 and Na-ZSM-5 but only the latter shows deactivation. There is even some conversion over silica but with HNCO observable from the beginning and produced in larger amounts than NH_3 below 340 °C. Experiments with deuterated nitromethane show that the reaction over Co/ZSM-5 has only a small kinetic isotope effect. However, there is rapid H/D exchange between methyl groups and water, most likely via the hydroxyl groups of aci-nitromethane, the enol tautomer of nitromethane. Hydrogen cyanide is a significant minor product over all three zeolite systems at temperature around 300 °C. With Co/ZSM-5 its concentration tracks that of ammonia during the course of deactivation and the subsequent enhancement of HNCO hydrolysis when water is added. Nitromethane reacts much faster with NO_2 than with NO and O_2 over all three zeolites with complete conversion at ≈ 220 °C to give almost entirely N_2 and CO_2 with Co/ZSM-5 and Na/ZSM-5 but with CO and N_2O formed as well over H-ZSM-5. NO_2 may act by removal of strongly adsorbed decomposition products (NH_3 or HNCO) since the reaction of NH_3 with NO_2 is very fast with Co/ZSM-5 and gives N_2 as the dominant product. The overall findings can be explained in terms of a scheme involving dehydration/hydrolysis reaction, largely on the aluminosilicate surface, followed by conversion of nitrogen-containing species to N_2 on the transition metal. They developed a reaction scheme which can explain the observation and its implications with respect to the possible involvement of nitrocompounds in the corresponding SCR reaction of higher hydrocarbons over other catalysts.

Ying et al. [59] investigated the nature of cobalt species in Co/ZSM-5: the catalyst for NO emission control. The chemical nature of Co^{2+} ion-exchanged ZSM-5 was studied by electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) and diffuse-reflectance Fourier-transform infrared spectroscopy (DRIFT). ESR and in situ XPS investigations show that the oxygen coordination geometry around the Co^{2+} at intersections or in channels of ZSM-5 does not have high symmetry and that Co^{2+} cations occupy at least two different sites in the zeolite pores. The oxidation state of Co^{2+} cations in ZSM-5 zeolites remains unchanged after being treated in oxygen at 450 °C, while the location and coordination of the Co^{2+} cations may be altered. In situ DRIFT studies of Co/ZSM-5 illustrate a strong interaction of Co^{2+} cations with coordinated molecular oxygen species, indicating a modification of the catalytically active sites in Co/ZSM-5 by oxygen or NO_2 under the simulated exhaust condition.

From many studies contributed to Co/ZSM-5 listed above, it can be understood that the utilization of Co/ZSM-5 appears to be the most appealing, especially since it can activate methane as the reducing agent. Unfortunately, Co/ZSM-5 based catalysts suffer from deactivation in the presence of water and sulfur dioxide, although in general they are more stable than Cu/ZSM-5. Metallosilicate based catalysts such as Co-silicate appear to overcome most of these problems, but face additional ones related to their lower activity for NO conversion and used non-methane, higher hydrocarbon as reducing agent. Efforts continue in this study to explore the development of Co based bimetallosilicate zeolites which can use methane as reductant and rise up the NO removal performance by adding two types of transition metal incorporated into the framework of MFI silicate so as to modify the proper acidity and redox properties for abatement of NO in exhaust gas.