

CHAPTER II

THE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES BY HYDROCARBONS ON PLATINUM GROUP METAL CATALYSTS UNDER LEAN-BURN CONDITIONS

Since the two pioneering works in 1990 [17, 18] independently discovering that either alkanes or alkenes were able to reduce NO on Cu-ZSM-5, not only in the presence of oxygen, but also that the reaction was favored in a large excess of oxygen, much research upon the selective catalytic reduction of NO by hydrocarbons under lean-burn conditions has been undertaken and subsequently published in the literatures [19-98]. The active catalysts reported so far can generally be classified into zeolites, metal oxides and noble metals. Within three groups of the catalytic systems, noble metals, especially platinum group metals, appear to be the most promising materials since they have already been used as the major component in conventional three-way catalysts and are known to have excellent thermal and hydrothermal stability as well as resistance to poisoning [112, 113, 140-142]. Also, they have been shown to exhibit enhanced NO reduction activity at low temperatures, typically lower than 300°C [116, 119, 120, 143]. This activity characteristic is of critical importance because a major percentage of the automotive exhaust emissions is released during the initial heating period of the engine as well-known to be namely 'cold start' problem. However, while they operate normally at low temperatures, which is an above benefit, there is an unfortunate side effect at these low temperatures, which is that a significant amount (sometimes the majority) of NO is converted to N₂O rather than N₂. N₂O, once formed, is not readily decomposed at these temperatures. Nevertheless, these catalysts do hold out promise and so a better understanding of their characteristic properties and likely mechanism of the selective catalytic reduction of NO under lean-burn condition could provide a valuable basis for the logical design of catalysts with enhanced properties.

At the present time, there is sufficient information available in the open literatures to begin to see patterns of behavior and to provide some insight into tentative reaction mechanisms. Therefore, the aim of this chapter is to critically

assess the experiment information currently available on platinum group metal catalysts under the heading of basic concept in the selective catalytic reduction of NO under lean-burn condition through kinetic results and to approach the obtained basic information for the useful application in practice. While the mechanistic studies of such reaction over platinum group metal catalysts will be separately reviewed in the next chapter.

At the beginning, a number of groups have investigated Pt, Pd and Rh catalysts, supported mainly on alumina or silica, using propane or propene as model hydrocarbon reductant [112, 122, 144-149]. There have also been a few results published on Ir and Ru catalysts [113, 150, 151] and for Pt, Pd and Rh on other supports or with other reductants [152-154]. Table 2.1 summarizes the main results, which have been published in the open literatures in a form, which makes comparison convenient or possible. The results in this table refer only to specific temperatures and it is important to recognize that the selective catalytic reduction of NO is very dependent on temperature [146], gas composition [155], choice of support [156, 157], type of reductant [135], etc., as reported later. However, in broad terms the results induced in Table 2.1 can be used to underline a number of important points.

With propene as a reductant, Pt was the best catalyst under experimental lean-burn conditions, although it produced a lot of N₂O and, indeed, this was a serious deficiency in Pt catalysts for this reaction. Where it was possible to make comparisons there seemed not to be much difference between Pt/Al₂O₃ and Pt/SiO₂ catalysts. Interestingly, Rh was moderately active for the formation of N₂ but this was only at a higher temperature range (ca. 300°C). Also, there was not much N₂O formed with Rh catalysts, which was consistent with the known properties of Rh under stoichiometric conditions [158]. It was noted that Pd was also not a very good catalyst irrespective of the choice of support.

When the reductant was propane, none of the platinum group metals was very selective or active. Where there was a reasonable activity, normally at higher temperatures, a substantial amount of N₂O was observed. It was interesting that in the case of the Pt catalysts with propane the Pt/Al₂O₃ showed some activity at higher temperatures, but Pt/SiO₂ appeared to be completely inactive [159].

Table 2.1 Catalytic activity and selectivity data for the selective catalytic reduction of NO on various supported platinum group metal catalysts

Catalyst [ref.]	NO (ppm)	HC (ppm)	O ₂ (%)	SV (cm ³ /min/gcat)	C _{NO} (%)	Temperature (°C)		
						200	250	300
Pt/B ₂ O ₃ /SiO ₂ /Al ₂ O ₃ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	24.7	10.2	6.3
					N ₂ O	25.0	6.7	2.7
Pt/AlPO ₄ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	17.9	5.8	4.0
					N ₂ O	14.5	6.3	5.1
Pt/AlPO ₄ -SO ₄ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	32.2	21.9	3.9
					N ₂ O	4.8	3.3	0.5
Pt/Al ₂ O ₃ [112]	995	C ₃ H ₆ (870)	5	160	N ₂	11.1	17.8	3.3
					N ₂ O	3.3	34.4	-
Pt/SiO ₂ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	12.0	8.0	5.0
					N ₂ O	40.0	21.0	14.0
Pt/Al ₂ O ₃ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	10.0	4.0	2.5
					N ₂ O	34.0	20.0	5.0
Pd/B ₂ O ₃ /SiO ₂ /Al ₂ O ₃ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	7.6	7.9	4.7
					N ₂ O	10.1	5.6	5.1
Pd/SiO ₂ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	0.0	3.0	2.0
					N ₂ O	2.0	9.0	6.0
Pd/Al ₂ O ₃ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	8.0	9.0	3.0
					N ₂ O	3.0	5.0	3.0
Ir/B ₂ O ₃ /SiO ₂ /Al ₂ O ₃ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	20.9	9.0	3.6
					N ₂ O	11.8	5.3	10.6
Ru/B ₂ O ₃ /SiO ₂ /Al ₂ O ₃ [113]	1000	C ₃ H ₆ (1000)	5	30-60	N ₂	20.3	6.0	-
					N ₂ O	4.2	0.2	-
Rh/Al ₂ O ₃ [112]	995	C ₃ H ₆ (870)	5	160	N ₂	4.4	8.9	42.2
					N ₂ O	0.0	2.2	4.4
Rh/SiO ₂ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	0.0	3.0	9.0
					N ₂ O	0.0	4.0	11.0
Rh/Al ₂ O ₃ [145]	1000	C ₃ H ₆ (918)	10	300	N ₂	3.0	22.0	22.0
					N ₂ O	1.0	5.0	9.0
Pt/Al ₂ O ₃ [118]	1079	C ₃ H ₈ (323)	10	62	N ₂	-	-	10.0
Pt/Al ₂ O ₃ [145]	1000	C ₃ H ₈ (973)	10	300	N ₂	1.0	-	14.0
					N ₂ O	3.0	-	12.0
Pt/SiO ₂ [145]	1000	C ₃ H ₈ (973)	10	300	N ₂	0.0	0.0	0.0
					N ₂ O	0.0	0.0	0.0
Pd/Al ₂ O ₃ [145]	1000	C ₃ H ₈ (973)	10	300	N ₂	0.0	3.0	12.0
					N ₂ O	0.0	2.0	12.0
Pd/SiO ₂ [145]	1000	C ₃ H ₈ (323)	10	300	N ₂	-	-	2.0
					N ₂ O	-	-	1.0
Rh/SiO ₂ [145]	1000	C ₃ H ₈ (323)	10	300	N ₂	-	-	1.0
					N ₂ O	-	-	1.0
Rh/Al ₂ O ₃ [145]	1000	C ₃ H ₈ (973)	10	300	N ₂	2.0	6.0	19.0
					N ₂ O	0.0	1.0	7.0

A comparison of the selective catalytic reduction of NO by propene on various platinum group metals is reproduced in Figure 2.1. These results can confirm the results from several published works summarized in Table 2.1, namely the relatively high activity of Pt even at low temperatures, and comparatively low activity of Pd, Rh and Ir. Hence, the next insight shall dominantly concentrate attention on Pt catalysts.

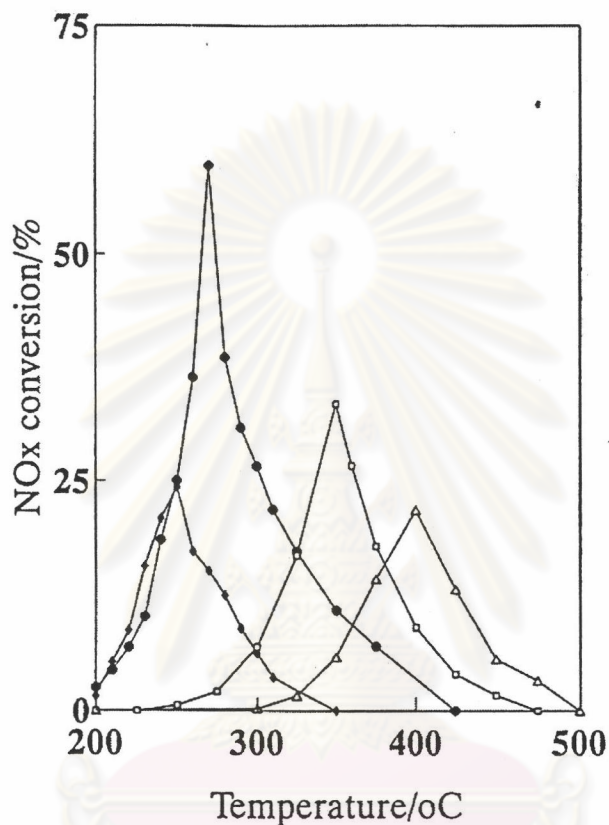


Figure 2.1 NO conversion as a function of temperature on various alumina-supported 1% platinum group metal catalysts: (●) Pt, (◆) Pd, (□) Rh, (△) Ir [160]

Focusing on Pt-based catalysts, the catalytic behavior towards temperature programmed reaction in the $C_3H_6+NO+O_2$ and $C_3H_8+NO+O_2$ systems over Pt/ Al_2O_3 is considered in Figure 2.2. Using propene as a reductant, conversions of C_3H_6 to CO_2 and NO to N_2 and N_2O both started at the same temperature, and raised with increasing temperature until 100% C_3H_6 conversion was reached. Maximum NO conversion occurred at this point. As the temperature was increased further the NO conversion to N_2 and N_2O decreased and conversion of NO to NO_2 began. The conversion of NO to NO_2 increased, went through a maximum and then decreased

with increasing temperature. On the other hand, the results on $C_3H_8+NO+O_2$ system were clearly very different from those obtained when propene was used as a reductant. The C_3H_8 light-off occurred at a higher temperature and was much less dramatic compared with that obtained with the alkene. Conversion of NO to NO_2 began at a lower temperature and occurred well before 100% C_3H_8 conversion was reached. The maximum NO conversion was not coincident with 100% C_3H_8 conversion being reached and was very much smaller than obtained using propene as the reductant. The above-mentioned behaviors are intrinsically general phenomena on Pt-based catalysts in the selective catalytic reduction of NO with propene and propane under lean-burn conditions [133, 134, 136].

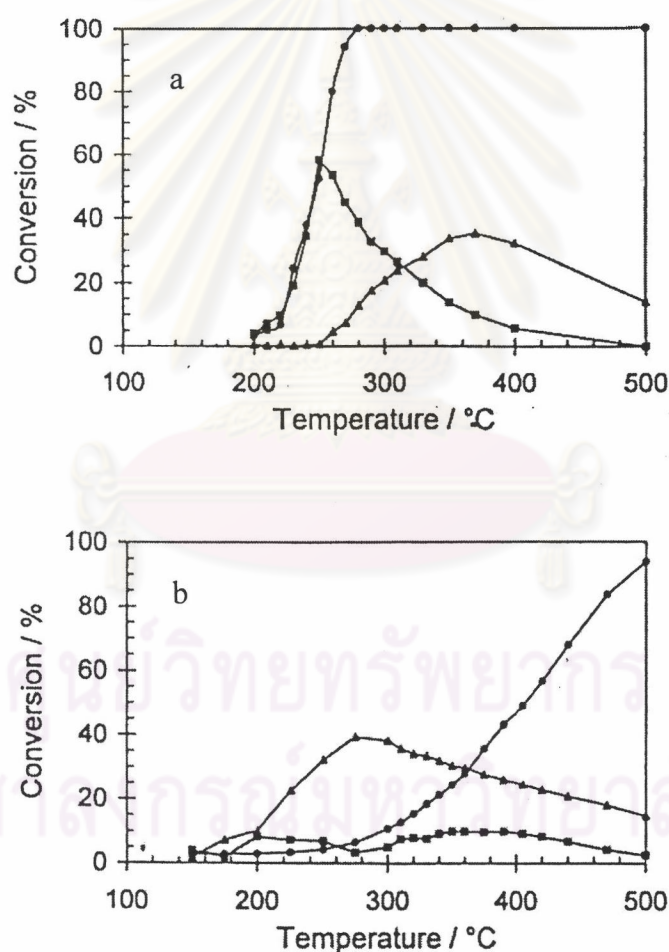


Figure 2.2 The effect of temperature on the selective catalytic reduction of NO over Pt/Al₂O₃ catalyst with (a) C₃H₆ and (b) C₃H₈ as the reductant: conversion of (●) HC, (■) NO to N₂ and N₂O, (▲) NO to NO₂ [136]

From the different catalytic behavior towards temperature programmed reaction obtained by changing types of reductant, typical results for Pt catalysts tested with a wide range of different organic compounds in some literature were interestingly pronounced [135, 153, 160]. The results in which the hydrocarbons have been varied from methane to hexadecane, ethene to 1-octene, methanol to 1-butanol and toluene through various xylenes to 1-methylnaphthalene are shown graphically in Figure 2.3. These results indicated that linear paraffinic hydrocarbons showed excellent NO conversion only at higher carbon numbers ($n > 4$ in C_nH_{2n+2}). The increasing effectiveness with increasing carbon number became smaller as 'n' increased so that n-heptane and n-hexadecane seemed to have identical properties. Curiously, the branched paraffin, 2,2,4-trimethylpentane, was much less effective. Olefinic compounds were much more effective than the corresponding paraffins and showed high activity and selectivity at low temperatures. Alcohols, with the exception of methanol, were very effective reductants. Aromatic compounds showed moderate NO conversion with the various xylenes being most effective followed by toluene but 1-methylnaphthalene was rather ineffective. Overall, the basic results showed that for a specific carbon number the order of efficiency increased as follows: isoparaffins < aromatics < n-paraffins < olefins = alcohols. The graphically conclusions about the NO conversion efficiency versus the C-number per molecule for hydrocarbon components tested are plotted in Figure 2.4.

No explanation was offered to account for the differences between, for example, isoparaffins and n-paraffins. However, it was found that there might actually be a simple correlation, which allowed for this variability to be rationalized. Figure 2.5 shows a plot of the temperature at which 20% of the reductant is oxidized to CO_2 against the temperature at which 25% of the NO is converted to reduced products (N_2+N_2O). It was clear that there was a rather good linear correlation between the effectiveness of the reductant and its combustion characteristics under the conditions of lean-burn experiments. This correlation held for the aromatic, linear and branched chain aliphatics, cyclic compounds, an alkene, and an alcohol. Interestingly, for the selective catalytic reduction of NO on a Pt catalyst the use of toluene as a reductant could give the capacity to reduce NO to N_2 with very high selectivity and without the formation of N_2O [161].

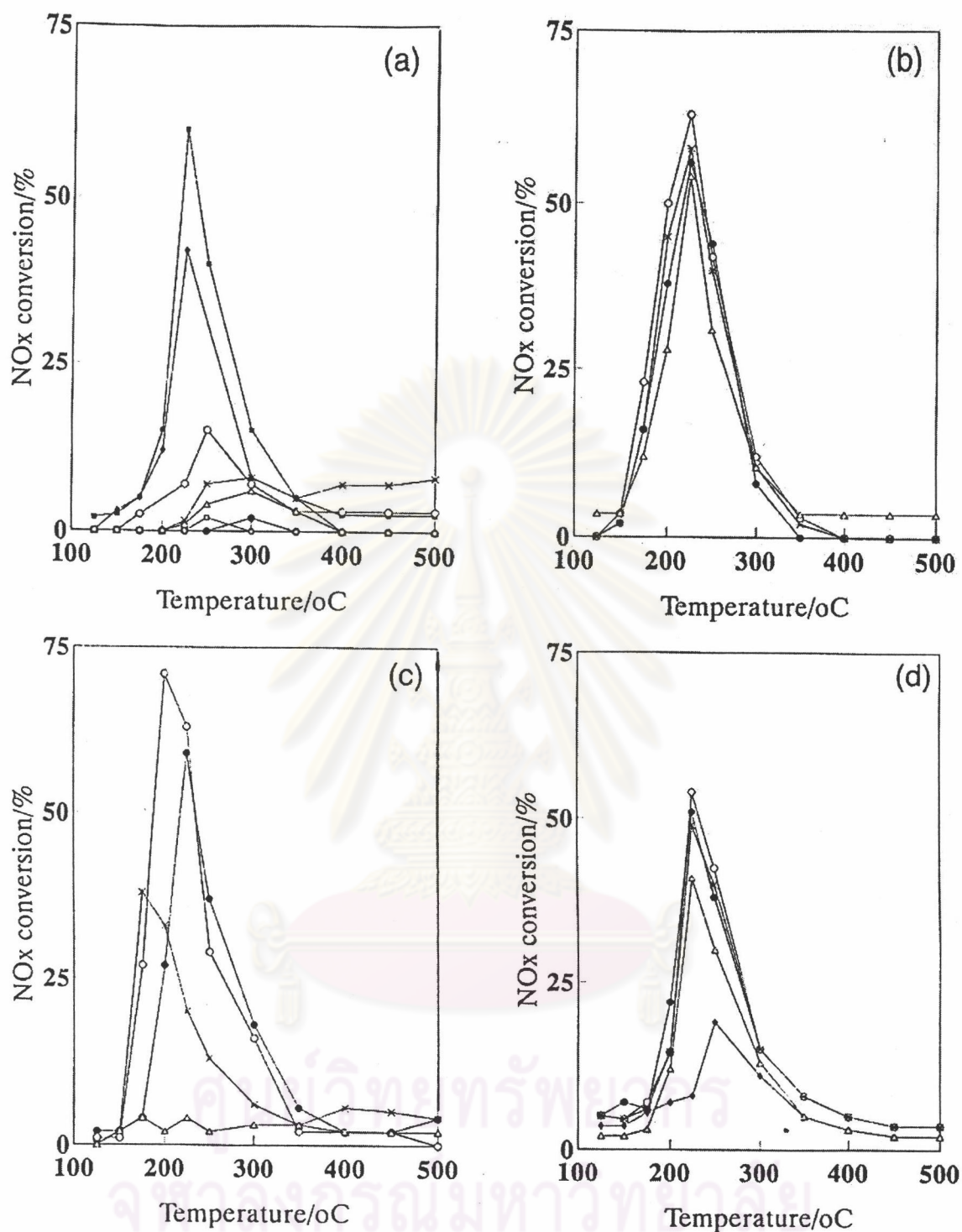


Figure 2.3 NO conversion on a Pt catalyst using various organic reductants. (a) Paraffinic hydrocarbons: (□) methane, (*) ethane, (●) propane, (△) n-butane, (◆) n-heptane, (○) isooctane, (■) n-hexadecane. (b) Olefinic hydrocarbons: (△) ethene, (*) propene, (○) 1-butene, (●) 1-octene. (c) Alcoholic compounds: (△) methanol, (*) ethanol, (○) 1-propanol, (●) 1-butanol. (d) Aromatic compounds: (△) toluene, (*) 1,2-xylene, (○) 1,3-xylene, (●) 1,4-xylene, (◆) 1-methylnaphthalene [135]

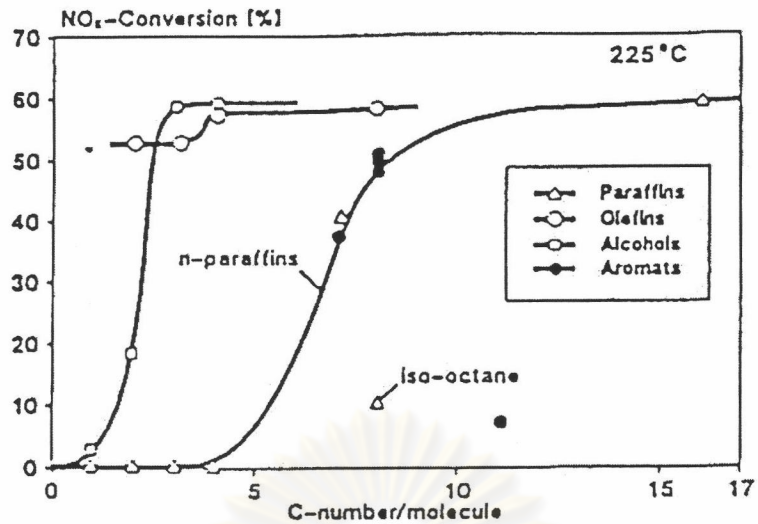


Figure 2.4 NO conversion as a function of the C-number per molecule for the different hydrocarbon species [135]

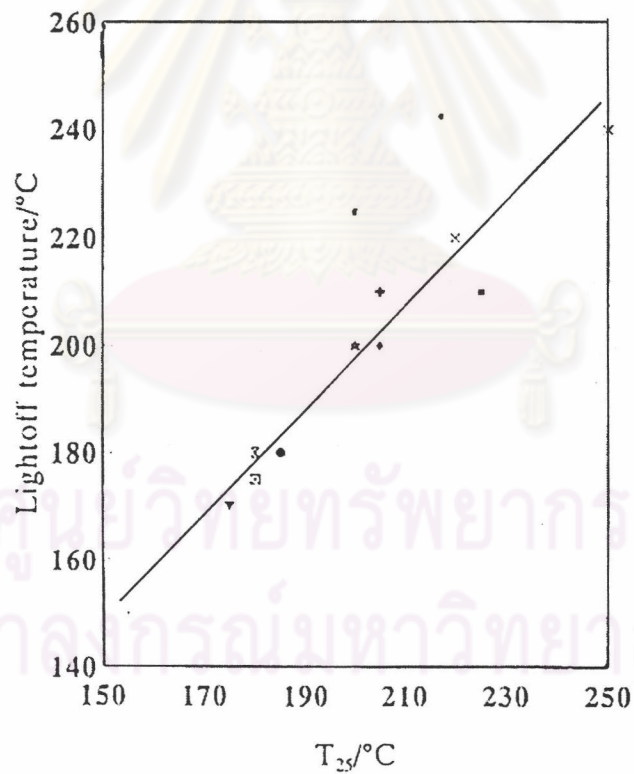


Figure 2.5 Light-off temperature (temperature at which 20% of reductant is oxidized to CO₂) versus temperature at which 25% conversion of NO occurs, for various reductants over both 1% Pt/Al₂O₃ and 1% Pt/SiO₂ catalysts [153]

The appropriate selection of type of platinum group metal with any reductant is mainly important to be useful for the fuel containing various components of hydrocarbons. Performances of Pt and Rh catalysts for the selective catalytic reduction of NO have been compared using various reducing agents to show the role of a same reductant on the different types of platinum group metal as seen in Figure 2.6. Although higher activities were attained when olefins were used for both Pt and Rh catalysts, the efficiencies of paraffins and oxygen-containing substances were higher in the case of only Rh catalyst. The consideration of choice of reductant coupling to a tested catalyst in order to obtain the excellent catalytic performance has generally appeared in the open literatures such as the use of Ag-based catalysts with alcohols [162, 163] or Co-ZSM-5 catalysts with methane [164-168] in the selective catalytic reduction of NO under excess oxygen.

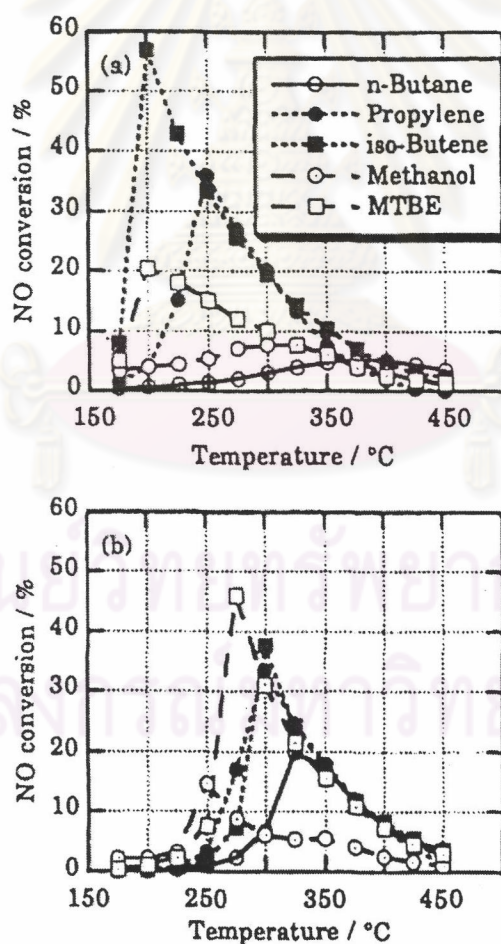


Figure 2.6 Effect of the reducing agent on NO conversion over (a) 6% Pt/Al₂O₃ and (b) 6% Rh/Al₂O₃ catalysts [152]

In most cases for the use of different reductants on Pt-based catalysts, with the exception of some paraffinic compounds, there was a close relation between the rate of oxidation of the hydrocarbon and the rate of NO reduction. Considering the use of propene as already shown in Figure 2.2, the reduction of NO began at the same time as the oxidation of propene. The two conversions then tended to rise together until the NO reduction reached a maximum close to the temperature at which the propene oxidation was complete. There seemed to be a clear link between the capacity of propene to reduce the catalyst and the activity for NO removal. When the peak activity in the NO conversion profiles is plotted against the temperature of this peak maximum, the relationship shown in Figure 2.7 is obtained.

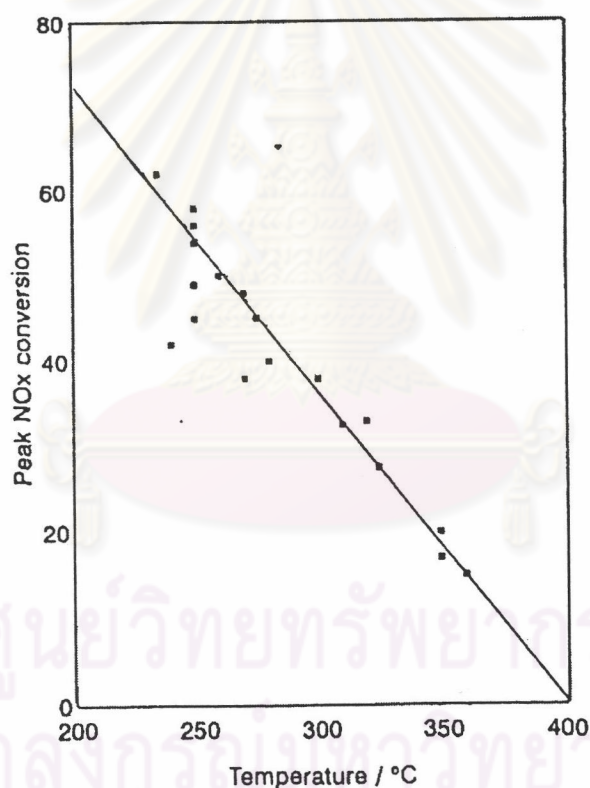


Figure 2.7 Variation of peak NO reduction with temperature for a range of supported Pt catalysts (a straight line shows trend for Pt/Al₂O₃ catalysts) [169]

These results showed that for a particular set of experimental conditions there was an upper limit to the NO conversion at any temperature. Presumably this reflected the changes in the relative rates of the C_3H_6/NO and C_3H_6/O_2 reactions, or in the relative rates of reoxidation of Pt by NO or O_2 , as the temperature was varied. These results suggested that unmodified Pt catalysts were likely to be limited in their capacity to selectively reduce NO in this temperature range. The real challenge will be to find ways of promoting the Pt to obtain a conversion above the limit seen in Figure 2.7.

The conversion of NO continued above the peak maximum temperature, but NO_2 became the predominant product. This was easily explained because the peak maximum in NO conversion corresponded quite closely to the temperature at which the combustion of the propene was complete. In fact, even though the gas mixture may contain some unburnt hydrocarbon there will be some surface sites, which remained fully oxidized, and so the formation of NO_2 can begin before the complete removal of the propene. Eventually, the formation of NO_2 was the only NO reaction observed and the amount of NO_2 formed was limited only by the thermodynamic equilibrium.

Also, the relationship between the NO reduction and the propene oxidation is largely responsible for the trend in NO conversion with Pt metal loading as shown in Figure 2.8. It was remarked that the propene oxidation curves were omitted for clarity but in each case they were parallel with the rise in NO conversion. As the metal loading was increased the activity per weight of catalyst increased and so the oxidation of propene set in at progressively lower temperatures. A parallel increase in activity for NO reduction meant that this reaction also commenced at lower temperatures as the Pt loading was increased. The increase in the activity for the NO reduction with increasing Pt content was not simply related to the change in the Pt metal area. The catalysts with higher Pt loading contained only a proportionately larger amount of Pt metal area whereas the increase in activity at the lower temperature was very much greater than this. There appeared to be a particle size effect with larger Pt particles having significantly higher turnover frequencies.

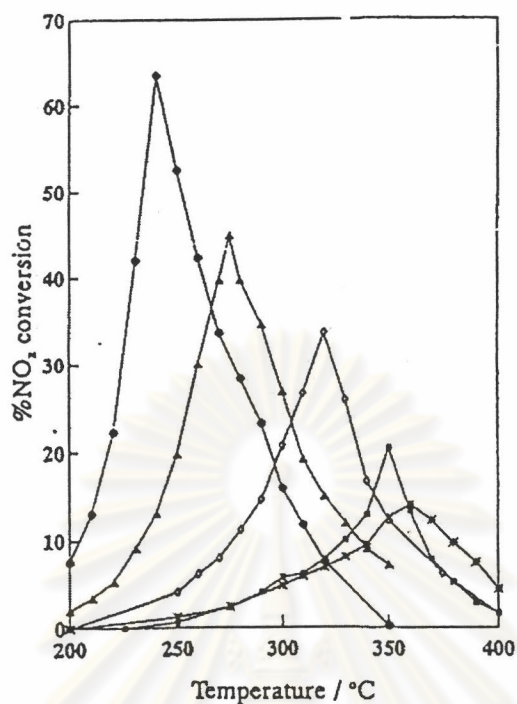


Figure 2.8 NO reduction as a function of temperature on Pt/Al₂O₃ catalysts with the different metal loading: (*) 0.1% Pt, (■) 0.25% Pt, (◇) 0.5% Pt, (▲) 1% Pt, (●) 2% Pt [116]

From the discovery that there was a small particle size effect because the increase in activity with Pt loading was larger than would be expected from the increase in Pt metal area [116], the study to the influence of metal particle size or metal dispersion on the NO reduction has extensively been reported [170-173]. The change of metal particle size could easily be proceeded by two general methods involving the variation of preparation conditions [146, 170-173] and the change of support or metal precursors [174, 175]. Considering the variation of preparation condition, series of alumina and silica supported Pt catalysts were prepared in which the average Pt particle size was adjusted by varying the calcination time and temperature for samples from a single batch of each catalyst [170]. The effect of Pt dispersion is shown for the alumina-supported and the silica-supported catalysts in Figure 2.9. The results appeared that there was little effect of metal dispersion for the alumina-supported catalysts over the range of average Pt particle sizes from 2.7 to 25 nm. In contrast, the Pt/SiO₂ catalysts did show some sensitivity to platinum

dispersion. On decreasing the dispersion from 39% to 1.8% (average Pt particle size increasing from 2.9 to 63 nm), the maximum NO conversion fell from about 80% to 50% and the temperature at which the maximum activity was seen moved from 210 to 250°C. However, the change in Pt surface area was much larger than this change in activity. It was also remarked that with the change of platinum particle size via the control in sol-gel processing [171], the effect of Pt dispersion on the reduction of NO was in agreement with the variation of calcination time and temperature.

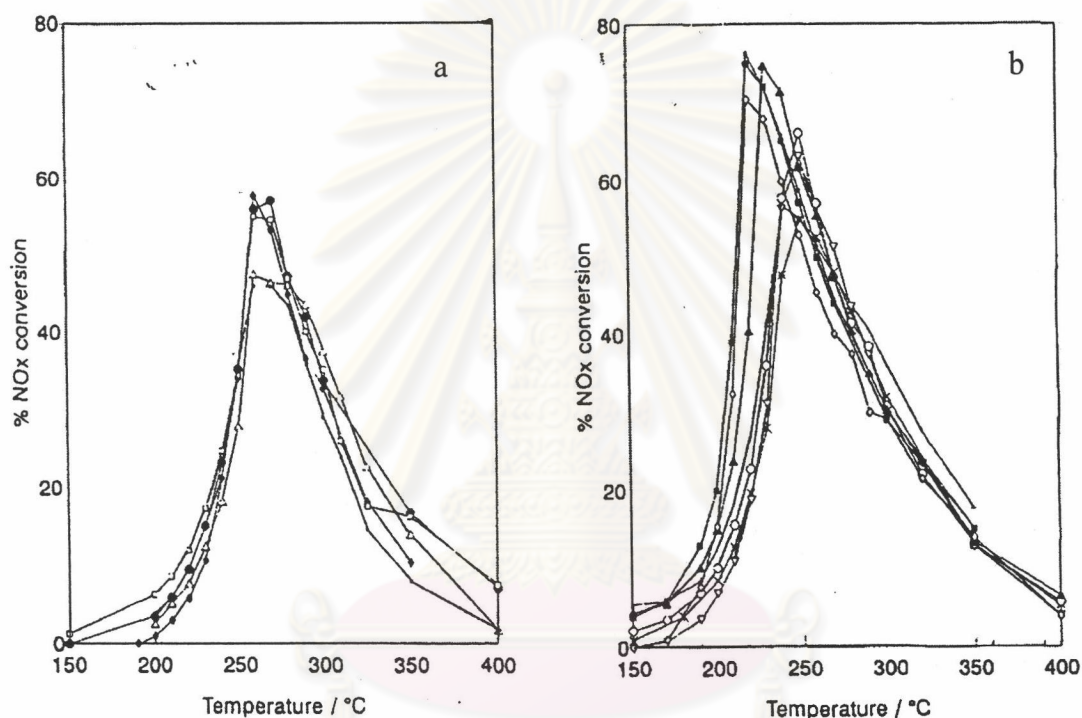


Figure 2.9 Effect of metal dispersion on NO reduction activity for (a) Pt/Al₂O₃ catalysts: (Δ) 4.6%, (\square) 6%, (\bullet) 9%, (\blacksquare) 42%, (\blacklozenge) 82% and (b) Pt/SiO₂ catalysts: ($*$) 1.8%, ($+$) 3.5%, (∇) 4.5%, (\circ) 6.5%, (\blacktriangle) 9%, (\diamond) 22%, (\blacksquare) 35%, (\blacksquare small) 39% [170]

This is best seen in Figure 2.10 which shows the calculated turnover frequencies (TOF) for the two sets of catalysts at temperatures at which the conversion is well below the maximum. These results showed that the TOFs for catalysts with 10% metal dispersion (corresponding to an average particle size of 11 nm) were approximately twice those of catalysts with 40% dispersion (3 nm). Below 5% dispersion (23 nm) the TOF increased rapidly indicating that very large particles

had a high specific activity. However, it should be noted that the increased activity per surface atom at low dispersion was offset by the decrease in the number of surface atoms as the average size of the metal particles increased. Interestingly, the dependence on Pt dispersion of TOF for NO reduction was much weaker than that of TOF for NO oxidation to NO₂ at low dispersion region [172, 176]. Thus, the NO reduction by propene did not involve NO oxidation for this case. Nevertheless, at much higher dispersion the difference of TOF for both reactions on Pt dispersion was rather similar leading to a significant role of NO oxidation to NO₂ on the reduction of NO. Hence, the reaction mechanism pathways in the selective catalytic reduction of NO by hydrocarbon under excess oxygen over Pt-based catalysts may be determined by the different metal particle size. The increase of intrinsic activity with decreasing dispersion has independently been confirmed by the change of support and metal precursors instead of calcination conditions in the preparation of various Pt particle sizes on catalysts as illustrated in Figure 2.11 [173].

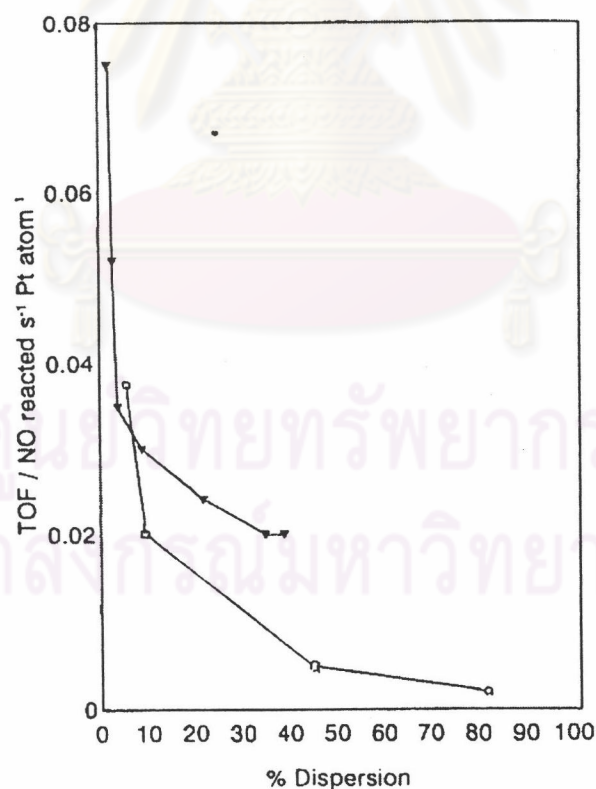


Figure 2.10 Turnover frequency as a function of platinum dispersion: (▼) Pt/SiO₂ at 210°C, (□) Pt/Al₂O₃ at 230°C [170]

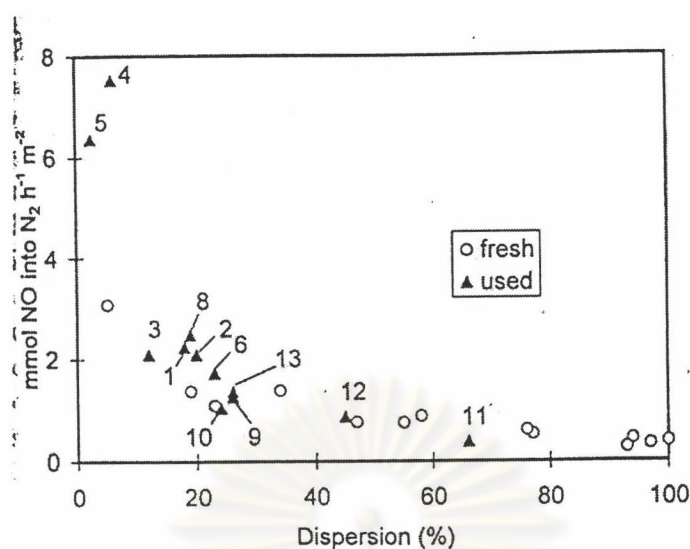


Figure 2.11 Maximum number of the amount of NO converted into N₂ per time and per surface area of accessible Pt as a function of Pt dispersion [173]

With the catalyst preparation by varying support and metal precursors to obtain the different metal dispersion, it was not only found that the Pt dispersion was a major factor affecting the intrinsic activity of the NO reduction by propene but also seen that the nature of the support (alumina or silica), the porosity and impurities of the support, and the nature of the platinum precursor were less important and not easily discernible. However, there still have been many works intending to exhibit the influence of these parameters on the NO reduction activity as well [174, 175].

The effect of platinum metal precursors, which were hexachloroplatinic acid, platinum nitrate as well as tetraammine platinum(II) hydroxide, and support metal oxides, which were zirconia, a base metal doped alumina, alumina as well as titania, on the catalytic activity for the conversion of diesel exhaust gas components was investigated [174]. The catalyst prepared from the tetraammine platinum(II) hydroxide precursor on the base metal doped alumina support showed the highest activity compared with the others for the conversion of the gaseous exhaust components. Nevertheless, the actual influence on the catalytic activity may not directly cause types of platinum metal precursor and support metal oxide, but the relative platinum particle size. The platinum particle size was not directly correlated to the lean NO_x activity, but could influence it indirectly through the hydrocarbon

light-off. Using a base metal doped alumina, alumina or titania as support the trend for the light-off temperatures for CO and HC versus the logarithm of the platinum particle diameter seems to be curved yielding a maximum in activity whereas using zirconia this trend seems to be linear as shown in Figure 2.12. It was believed that on small particles the number of these multi-atom sites dropped sharply thereby lowering the specific activity for HC conversion while on larger particles such sites were more common but the total platinum surface area became smaller thereby also lowering the specific activity. This observation differed from the above results in which the larger metal particle size became the higher specific NO reduction activity appeared [170, 173]. This might be due to the use of n-hexadecane as a reductant instead of propene.

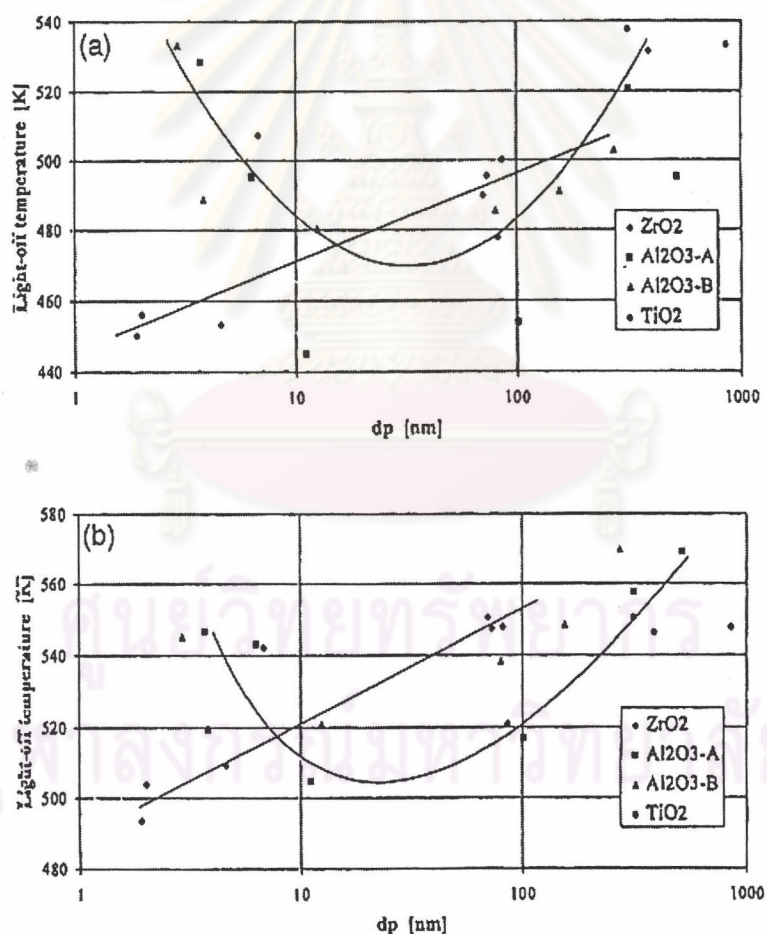


Figure 2.12 Light-off temperature for (a) CO and (b) HC versus the platinum particle size as determined with CO chemisorption for the different support oxides [174]

The intrinsic influence of metal precursor on the NO reduction activity was also reported by the preparation of Pt/Al₂O₃ catalysts from five different types of metal precursors, which were controlled to obtain the same metal dispersion [116]. These metal precursors involved dinitro-diammine-Pt, tetraammine platinum hydrogen carbonate, tetraammine platinum dichloride, tetraammine platinum acetate and hexachloroplatinic acid. It was found that the Pt-based catalyst prepared by tetraammine platinum hydrogen carbonate precursor showed the highest NO reduction activity with propene whereas the lowest activity occurred from the use of hexachloroplatinic acid as a precursor. Hence, the NO reduction activity might be enhanced by using the effective precursor. For example, the N₂/N₂O selectivity could be improved by using the organoplatinum complexes such as PtMe(OPh)(cod) (cod = 1,5-cyclooctadiene) as the precursors better than an inorganic platinum salt [175].

The effect of changing the support on the activity of the Pt for the selective catalytic reduction of NO with hydrocarbons has been investigated by several groups, especially the change from alumina to silica with Pt catalysts [136, 146, 173]. In general, the silica-supported catalyst is somewhat more active than the corresponding alumina-supported catalyst and also perhaps less selective for the formation of N₂O [136]. In order to more closely compare the activities of alumina- and silica-supported catalysts, two sets of catalysts were prepared from the 1% Pt samples by adjusting the calcination treatment so as to obtain catalysts on each support having dispersions of ca. 10% and ca. 40%. The activities towards temperature profiles for both dispersion catalysts are shown in Figure 2.13. The silica-supported catalysts were clearly more active in both cases. Consequently, there was a real support effect although whether this was a primary effect-the support was directly involved in the reaction-or a secondary support effect-the support modified the true active phase-was not clear. It was certainly possible that Pt particles on the two supports could have different morphologies and this could account for differences in activities if, for example, the reaction proceeded more rapidly on smooth surfaces.

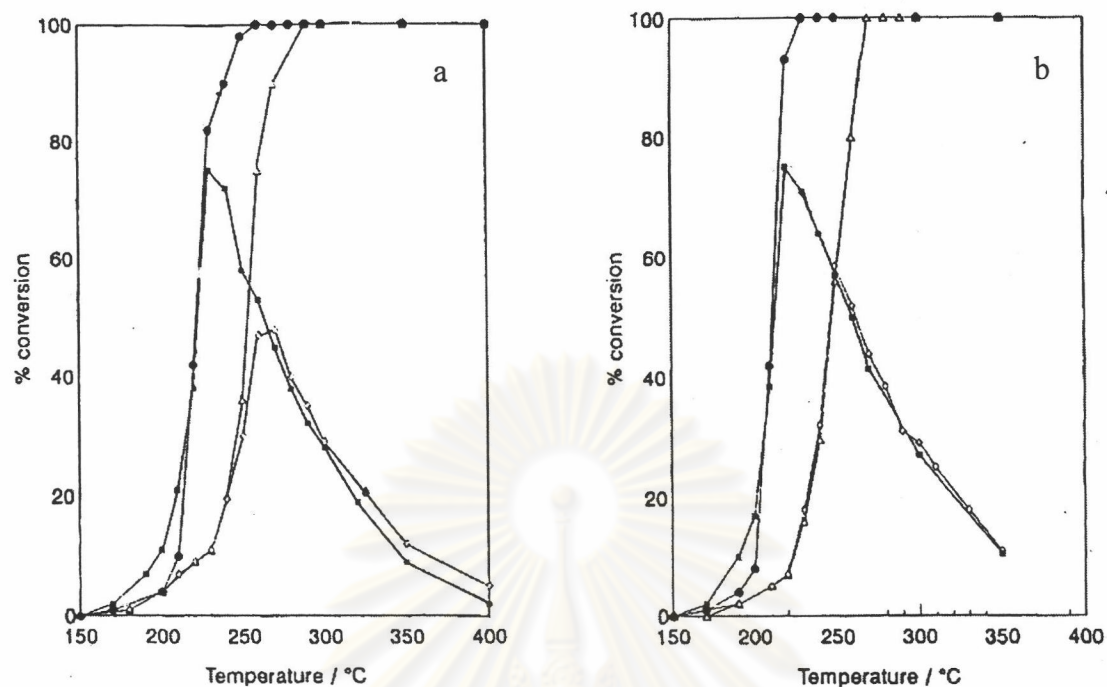


Figure 2.13 NO reduction and C₃H₆ oxidation as a function of temperature for Pt catalysts with (a) 10% metal dispersion and (b) 40% metal dispersion: (■) Pt/SiO₂ (NO), (●) Pt/SiO₂ (C₃H₆), (◇) Pt/Al₂O₃ (NO), (△) Pt/Al₂O₃ (C₃H₆) [170]

The comparison between alumina- and silica-supported catalysts has been extended to Pd and Rh [146]. Figure 2.14 shows the NO conversion versus the reaction temperature for these catalysts. The results showed that for each of metals, the silica-supported catalysts were more active than those on alumina, although with Pd the difference was rather small. The metal dispersions (Pt/Al₂O₃, 41%; Pt/SiO₂, 35%; Pd/Al₂O₃, 28%; Pd/SiO₂, 19%; Rh/Al₂O₃, 51%; Rh/SiO₂, 49%) were sufficiently close, given the small effect of particle size in this range noted above, that this would not, by itself, account for the higher activity of the silica-supported catalysts. However, these results were somewhat at odds with those reported by some literature [145] in which for example, it was found that Rh/Al₂O₃ was much more active than Rh/SiO₂. It did not have an explanation for these differences in relative activities but the sensitivity of NO reduction reaction to experimental conditions might be a contributing factor.

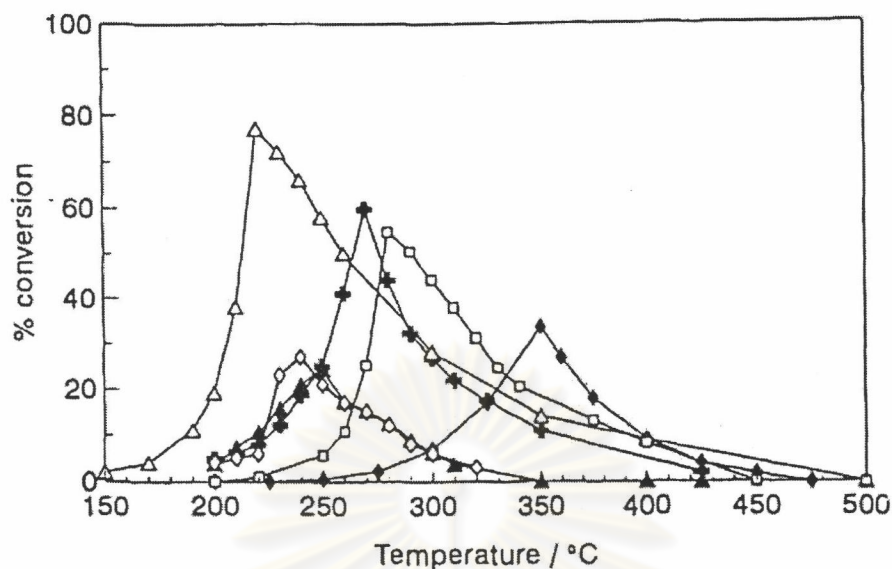


Figure 2.14 NO reduction as a function of temperature for platinum group metal catalysts: (■) Pt/Al₂O₃, (△) Pt/SiO₂, (◆) Rh/Al₂O₃, (□) Rh/SiO₂, (▲) Pd/Al₂O₃, (◇) Pd/SiO₂ [146]

Figure 2.15 shows the variation in the activity for the NO reduction reaction on various metal oxide-supported 1% Pt catalysts. It indicated that many of the catalysts involving alumina, zirconia, tin(IV) oxide and tungsten(VI) oxide had very similar activities (approximately 50% NO conversion at 250°C). The 1% Pt/TiO₂ was less active and the peak maximum occurred at a higher temperature, whereas the 1% Pt/SiO₂ was more active and had a maximum conversion at a lower temperature. Although 1% Pt/MgO was active for both NO reduction and propene oxidation at 250°C, it was considerably less selective for NO reduction than any of the other catalysts, which were active at this temperature.

From the discovery that the interaction between metal and support directly affected the intrinsic NO reduction activity, attempt to change the support from alumina or silica to others in order to improve the catalytic performance of Pt-based catalysts has currently been exhibited. A group of zeolite supports was given particular attention to substitute alumina. Examples of the selected zeolite-type supports were ZSM-5 [177-180], dealuminated Y (DeY) [181], USY [182] and MCM-41 [183-185]. The experimental investigation on the catalytic activity for

HC+NO+O₂ reaction systems under highly oxidizing conditions and comparison with that of Pt/Al₂O₃ or Pt/SiO₂ indicated the similar kinetic behavior of the two groups of supports. These suggested that the role of zeolite-type support might not be so critical in determining the catalytic activity of the Pt-based catalysts for lean NO_x reduction. However, all zeolite-type supported Pt catalysts provided higher specific NO reduction activity than alumina- and silica-supported Pt catalysts although the high selectivities were still observed toward the formation of N₂O. It was also noted that the significant advantage of the cooperation between zeolite-type supports and platinum was that water vapor and sulfur dioxide had a relatively small effect on the NO reduction activity of these catalysts.

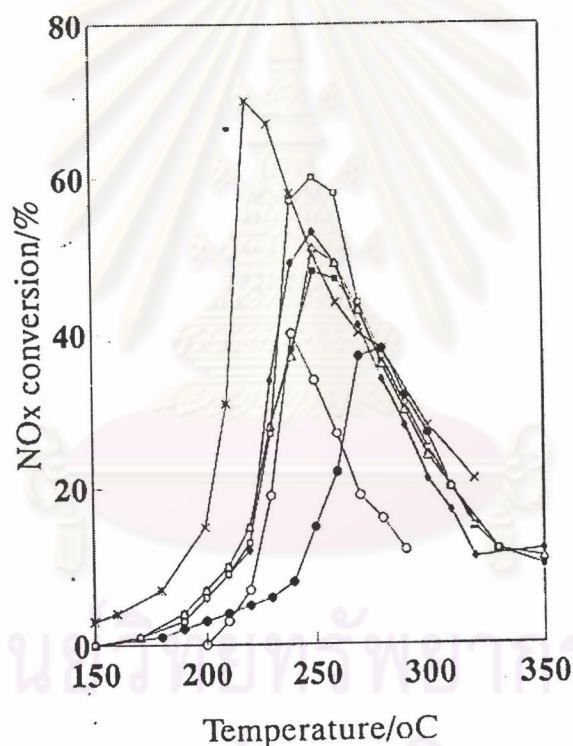


Figure 2.15 NO reduction as a function of temperature on different metal oxide supported Pt catalysts: (□) Pt/Al₂O₃, (*) Pt/SiO₂, (△) Pt/ZrO₂, (●) Pt/TiO₂, (■) Pt/SnO₂, (◆) Pt/WO₃, (○) Pt/MgO [160]

Another interesting feature of Pt-based catalysts is their activity for the oxidation of hydrocarbon in the presence and in the absence of NO. Figure 2.16 shows these results with propene comparing between silica- and alumina-supported Pt catalysts. In the absence, or in the presence of NO, the silica-supported catalyst was

considerably more active with the reaction commencing at a temperature about 50°C lower. More interestingly, however, was the fact that when NO was present, even at a much lower concentration than the O₂, the oxidation of propene was seriously inhibited, the temperature for any particular percentage conversion increasing by about 50°C. These results seemed to suggest that even though the dissociative adsorption of oxygen was expected to be very fast under these experimental conditions and so the adsorption of NO would be expected to be very inhibited, there was a strong interaction or competition between oxygen and NO for surface sites. The oxidation of an alkene was normally so facile that it was possible that reoxidation, or perhaps, more likely, desorption of H₂O from surface sites was rate determining. The two steps were, of course, interdependent since readsorption of oxygen could not occur until OH groups were removed from the surface. If NO adsorption could inhibit either of these desorption/readsorption steps it would account for the lower activity for propene combustion.

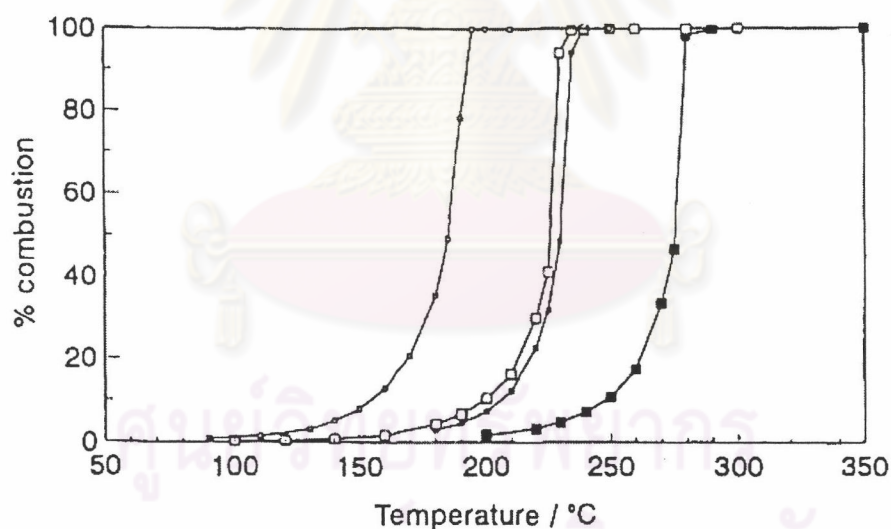
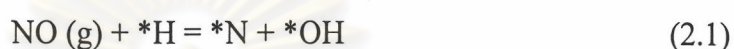


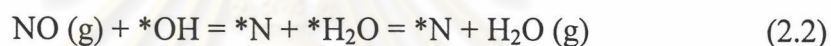
Figure 2.16 C₃H₆ oxidation as a function of temperature in the presence and absence of NO: (□ small) Pt/SiO₂ without NO, (□) Pt/SiO₂ with NO, (■ small) Pt/Al₂O₃ without NO, (■) Pt/Al₂O₃ with NO [146]

This possibility raises an interesting point concerning the mechanism of NO reduction on Pt under lean-burn conditions and this will be addressed more fully in the next chapter. However, it is worth raising the question here as to whether the adsorption of NO in competition with O₂ is facilitated by the surface OH groups

which must be present in a steady state equilibrium with the gas phase. The work reported to the enhancement of the reaction between NO and CO by hydrogen and water over Pt-containing catalysts was considered to explain these [186]. Although such work was concerned with the conventional stoichiometric reaction conditions, there was possibly a similarity to the reaction under lean-burn conditions. It was shown that the addition of hydrogen or water to a stoichiometric mixture of CO and NO could significantly enhance the conversions of both NO and CO. One suggestion was that NO dissociation was hydrogen assisted, e.g.,



Under the lean-burn conditions it might be more appropriate to write this in the form:



or even as a non-dissociative adsorption, given the comparatively low temperatures.



Such a species could explain the inhibition of propene oxidation by limiting the amount of available active sites (Pt-O_s) while at the same time being consistent with the fact that no NO₂ was observed when there was propene in the gas mixture. Another fact that might support this suggestion of enhanced adsorption of NO when OH was present was that with the conventional hydrocarbon combustion catalysts the water was a severe poison, especially at the temperatures used in the general NO reduction experiments. It seemed that surface OH groups were quite stable on the surface of platinum group metals at temperatures below about 250°C [170].

The kinetic information about effects of concentrations of NO, C₃H₆ and O₂ on the catalytic activity for the selective catalytic reduction of NO by C₃H₆ is an important basis, which can not be negligible. Most of literatures reported to the results in the same direction. The effect of varying NO concentration on NO reduction, C₃H₆ oxidation, as well as N₂ selectivity on Pt/Al₂O₃ is shown in Figure 2.17. An increase in both the conversions and a decrease in N₂ selectivity with

decreasing NO concentration were observed. The apparent reaction orders were found to be zero for NO reduction and negative for C_3H_6 oxidation. The zero-order dependence of NO reduction on the concentration of NO for Pt/ Al_2O_3 could imply the non-participation of NO in the rate-determining step of NO reduction. The negative dependence in NO on the rate expression for the oxidation of C_3H_6 could be interpreted by inhibition of reductant oxidation due to the presence of strongly adsorbed NO. This was indeed observed to be the case, since the presence of NO was found to cause a significant upshift in the activity curve for C_3H_6 oxidation as already shown in Figure 2.16.

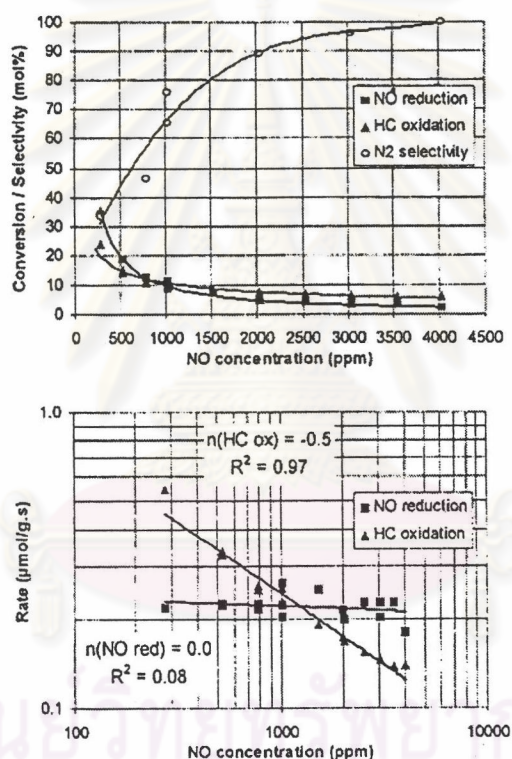


Figure 2.17 NO concentration effect on the selective catalytic reduction of NO containing NO reduction, C_3H_6 oxidation and N_2 selectivity on Pt/ Al_2O_3 catalyst [148]

The effect of varying C_3H_6 concentration on the NO reduction, C_3H_6 oxidation and N_2 selectivity on Pt/ Al_2O_3 is shown in Figure 2.18. A decrease in activity for both reactions and an increase in N_2 selectivity with increasing C_3H_6 concentration were obtained. It should be noted that the activities for the lowest tested C_3H_6 concentration values of less than 500 ppm were found to deviate significantly from

'differential' kinetics. Thus, the accuracy of those data points would be questionable. The negative orders of both the reactions with respect to C_3H_6 were found and the two reaction rates were essentially equal to each other. This observation appeared to indicate activation of the reductant by dissociative adsorption, possibly leaving strongly adsorbed fragments of the reductant on the active sites. At low temperatures reductant activation would be kinetically limited. Therefore, the increased formation of such strongly adsorbed fragment by increasing the reductant concentration would practically lead to a poisoning phenomenon [119].

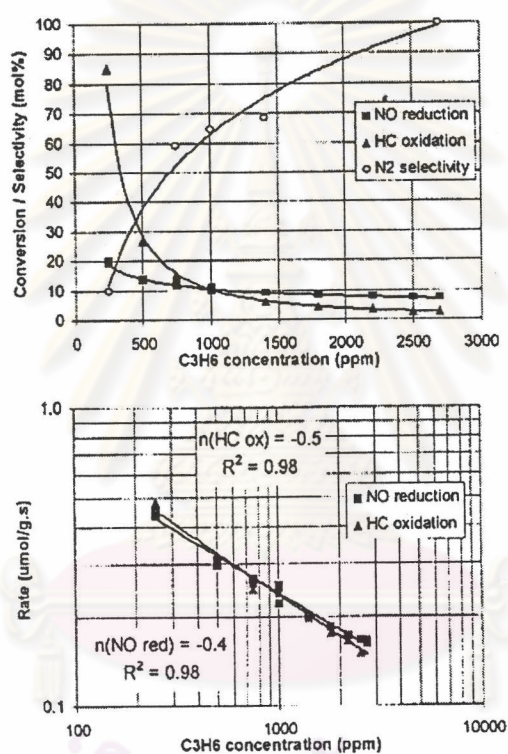


Figure 2.18 C_3H_6 concentration effect on the selective catalytic reduction of NO containing NO reduction, C_3H_6 oxidation and N_2 selectivity on Pt/Al_2O_3 catalyst [148]

The effect of varying O_2 concentration on the NO reduction, C_3H_6 oxidation and N_2 selectivity on Pt/Al_2O_3 is shown in Figure 2.19. A linear increase in both the conversions was observed, as well as a decrease in N_2 selectivity with increasing O_2 concentration. The apparent reaction orders were found to be positive for both the reactions and the measured reaction rates were practically equal to each other. The positive order dependence of NO reduction and C_3H_6 oxidation on O_2 for Pt/Al_2O_3

indicated that at low temperatures, even under excess oxygen, the reductant was selectively oxidized by NO and there were therefore no significant competitive oxidation to lead to a poisoning effect of oxygen on the NO reduction activity.

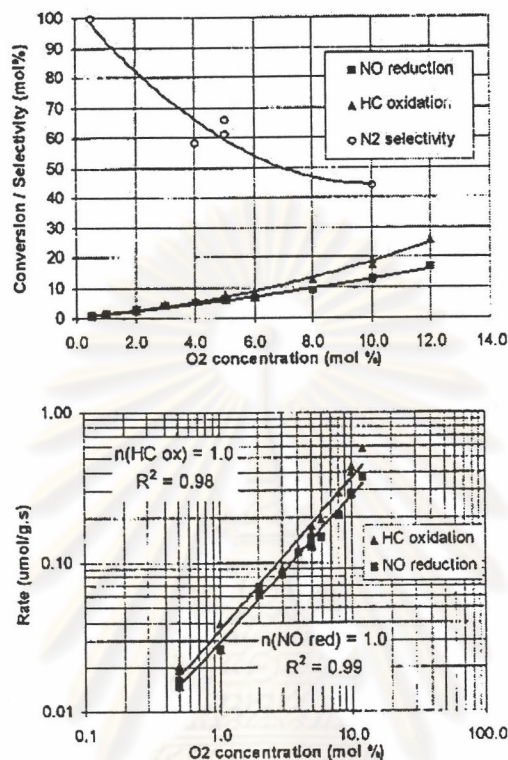


Figure 2.19 O₂ concentration effect on the selective catalytic reduction of NO containing NO reduction, C₃H₆ oxidation and N₂ selectivity on Pt/Al₂O₃ catalyst [148]

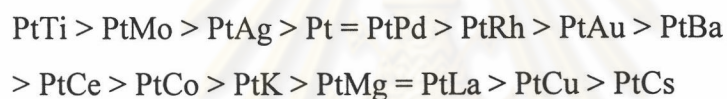
The obtained available information about the basic catalytic behavior can encourage in the development of new catalyst formulations sufficiently active and selective for the proposed process capable to meet the continuously increased requirements for a clean environment. Especially, the selectivity towards N₂ formation rather than N₂O is an important index of catalyst performance. Efforts thus far on improving the catalytic properties of Pt-based catalysts for the selective catalytic reduction of NO by hydrocarbons under excess oxygen can be currently summarized as follows:

1. Using direct promoters in direct interaction with the catalyst active phase or doping the catalyst supporting material with additives. Rh was the first in the list of

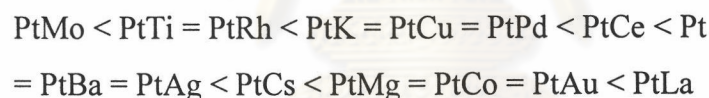
such promoting efforts due to its property to easily decompose N_2O . Hence, the performance of binary platinum-rhodium catalysts was examined in the previous work [112]. It was found that there was an optimum catalytic composition of Pt and Rh giving the highest NO conversion. However, under that composition, the selectivity toward N_2 was still low and the catalytic properties of binary catalyst were similar to those of simple platinum catalysts. The use of Pd, Ir or Ru instead of Rh resulted in a large production of N_2O as well [187].

With the unsuccessful results for adding Rh, a series of Pt/ Al_2O_3 promoted by metal oxides (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo and Ti) or noble metals (Ag, Au, Pd and Rh) were prepared and tested for the lean NO_x reaction using C_3H_6 as a reductant [139]. It was found that the promoters had a significant effect (beneficial or otherwise) on the activity and temperature range of operation of Pt/ Al_2O_3 as follows:

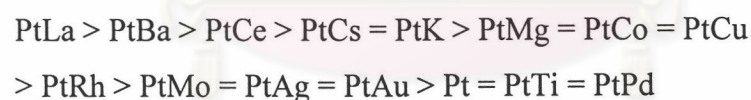
a. The maximum NO_x conversion



b. The temperature at which maximum NO_x conversion occurred



c. The full width of the NO_x conversion curve at half of maximum conversion



However, there was no promoter to distinctly give an extremely catalytic performance. Subsequently, some literatures [188-190] have reported that in the presence of Zn on Pt-based catalyst the NO conversion was increased in parallel with the N_2 formation. Moreover, the range of temperature in which N_2 was formed was larger than in the absence of Zn.

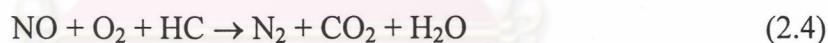
Attempt to combine three or four components of metal for promoting the catalytic activity was also proceeded [191, 192]. The simultaneous addition of Mo and Na to Pt/ SiO_2 catalysts showed that the temperature window on the selective catalytic reduction of NO was wider and shifted at higher temperature than that on bimetallic PtMo/ SiO_2 and monometallic Pt/ SiO_2 catalysts under lean static conditions. The data of XPS, IR and CO adsorption also indicated that the oxidation of Pt on

PtMoNa/SiO₂ catalysts was depressed by the added Mo and Na even under excess oxygen conditions, so that the reaction characteristics of trimetallic PtMoNa/SiO₂ catalysts were improved [191].

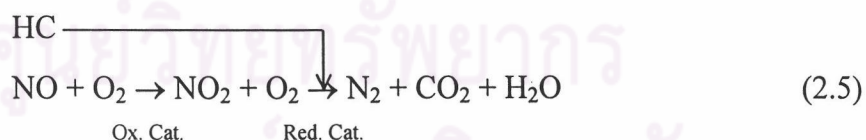
2. Developing a new procedure in the catalyst preparation to change the catalytic properties. Example of this method is the single-step sol-gel technique instead of the conventional impregnation technique [193, 194]. It was found that the N₂ selectivity of a sol-gel Pt-based catalyst was higher than that of an impregnated catalyst. Additionally, the sol-gel catalysts showed remarkable robustness after exposure to high temperature, sulfur dioxide and long time exposure to reactants.

3. Increasing the hydrocarbon reductant into the reaction system to assist selectively the reduction of NO. Typically, the introduction of hydrocarbon can be divided into two methods involving the injection into the reactant stream and the doping on the catalyst support. The former is the procedure known in the name of intermediate addition of the reductant (IAR) method [195-197]. The concept of this technique can be described as follows:

Conventional HC-SCR



IAR method



The IAR method is revealed to prevent the combustion with O₂ or wasting of hydrocarbons on oxidation sites. In general, this process has coupled with the development and design of bifunctional catalysts [198, 199]

The latter method is the direct doping of hydrocarbon reductant on the catalyst support. The used hydrocarbon in this case may be in form of various types of carbonaceous species, i.e., coke [200], soot [201] and activated carbon [202]. These

carbon-containing species promoting the reduction of NO at high temperature independently resulted in the broadness of the temperature window of operation.

However, in spite of extensive research efforts involving the kinetic results for the selective catalytic reduction of NO under lean-burn condition on Pt-based catalysts in the past years, this procedure is still inefficient and has not yet been widely employed in practical application. This may be due to the rational argument of two candidate groups independently suggesting the different reaction mechanism. Therefore, the clarification of the reaction mechanism is essential for future improvement of this catalytic process. Hence, the mechanistic studies of such reaction on platinum group metal catalysts are individually reviewed in the next chapter.

