

CHAPTER III

MECHANISTIC STUDIES

There have been a number of studies in which the mechanistic aspects of the selective catalytic reduction of NO by hydrocarbons under excess oxygen on Pt-based catalyst have been considered but as yet there is little definitive evidence in support of one model rather than another and as a consequence several mechanisms have been proposed. In general, the reaction mechanism can be roughly subdivided into decomposition mechanism and reduction mechanism. The former, in which N_2 is considered to be formed by NO decomposition over an oxygen-deficient surface created by hydrocarbon oxidation, is originated from the discovering that Cu-ZSM-5 shows excellent activity for both NO decomposition and the present reaction. On the other hand, the reduction mechanism accounts for the formation of N_2 by a series of reaction step containing a reaction between two chemical species. In this respect there have been several proposals such as the reaction of NO and the deposited carbonaceous material formed from hydrocarbon, the reaction of NO and the partially oxidized hydrocarbon and the reaction of hydrocarbon and NO_2 formed by oxidation of NO. However, the basis of reduction mechanism seems to be three important factors for the selective catalytic reduction of NO to occur. These are activation of the hydrocarbon, activation of oxygen and selective reaction of an intermediate with NO_x in preference to oxygen. In this chapter, the extensive mechanistic studies of Pt-based catalysts for the selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen are reviewed in detail.

3.1 NO Decomposition Mechanism

In 1994, the NO decomposition mechanism for the selective catalytic reduction of NO by hydrocarbon under excess oxygen was first proposed with Pt-based catalyst by using temporal analysis of products (TAP) technique [116]. In this procedure, it was possible to investigate reactions on a time-scale of milliseconds, and by using very small gas pulses of different compositions and separated by different

time intervals it was possible to assess the extent to which different types of surface intermediate might be involved in the reaction.

Figure 3.1 demonstrates that on a prerduced $\text{Pt}/\text{Al}_2\text{O}_3$ surface NO dissociation leads to the formation of N_2 but that the amount of N_2 formed decreases, as the number of pulses of NO introduced is increased. It was easily shown that this self-poisoning was due to the retention of adsorbed oxygen, even at 400°C . Pulse-probe experiments in which adsorbed oxygen was removed by introducing a second pulse of either H_2 or CO immediately after the NO pulse showed that the initial activity of the fully reduced Pt was completely stable providing all the surface adsorbed oxygen was removed between the successive NO pulses. Moreover, by adjusting the time interval between the introduction of the NO pulse and the pulse of reductant (CO and H_2) in the range 0.1-10 sec, it was also possible to show that there was no direct interaction between the NO and the reductant.

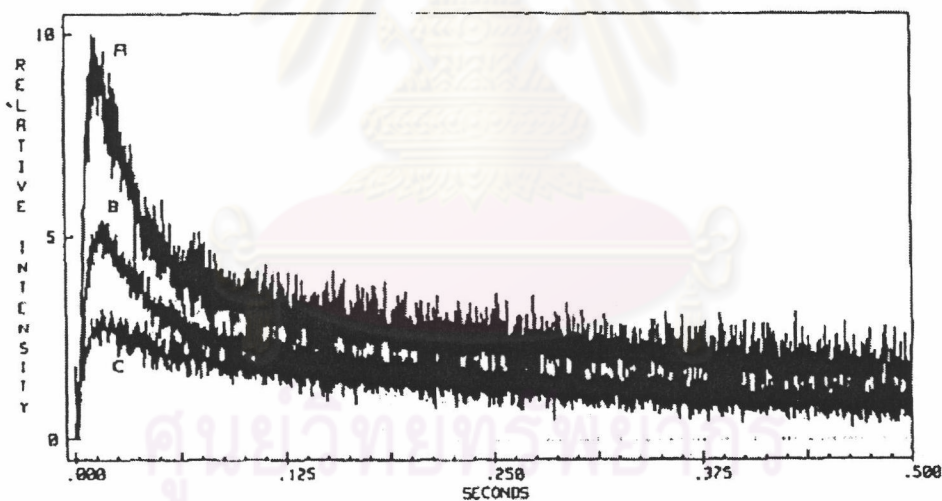


Figure 3.1 Variation of N_2 yield with number of NO pulses over reduced $\text{Pt}/\text{Al}_2\text{O}_3$ at 400°C : (A) average of pulses 1-10, (B) average of pulses 11-50, (C) average of pulses 51-90 [116]

Figure 3.2 demonstrates this point for NO- H_2 pump-probe experiments. It was seen that irrespective of the time interval between the two pulses the amount of N_2 produced was constant. Moreover, for the first experiment, where the time interval was only 0.1 sec between the introduction of a pulse of H_2 and the subsequent

introduction of the NO pulse, there was still some adsorbed hydrogen on the Pt when the NO pulse reached the catalyst. Consequently, the fact that the amount of N_2 produced was the same as for an experiment where all the hydrogen had been desorbed, showed that there was no direct reaction between NO and adsorbed hydrogen on such fully reduced surfaces.

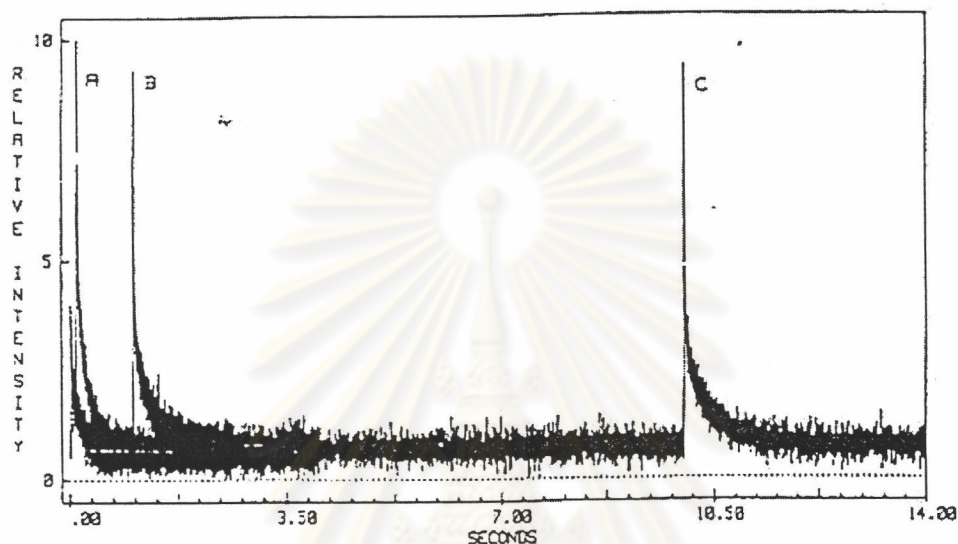


Figure 3.2 Variation of N_2 yield with the interval between H_2 and NO pulses: (A) 0.1 sec, (B) 1 sec, (C) 10 sec [116]

When these pulse-probe experiments were performed by using C_3H_6 and C_3H_6/O_2 mixtures as the reductant, the two interesting features emerge as shown in Figure 3.3. First, it was seen that the C_3H_6/O_2 mixture, even though this could be an overall oxidizing mixture was effective at leaving the Pt surface active and stable for the conversion of NO to N_2 . Second, when C_3H_6 was used without O_2 , the catalyst became self-poisoned due to deposition of carbonaceous material on the Pt. This would suggest that carbonaceous layers were not important in the selective NO reduction reaction on these catalysts. Moreover, it was possible that an important role of oxygen in the $C_3H_6+NO+O_2$ reaction was to prevent self-poisoning of the Pt by carbonaceous residues. Comparison between C_3H_6/O_2 and either CO or H_2 as reductants in Figure 3.4 shows that the C_3H_6/O_2 is rather better. The differences in the amount of N_2 produced were not great, but may be significant nevertheless in

terms of the overall mechanism in a steady state kinetic experiment as compared to these transient conditions.

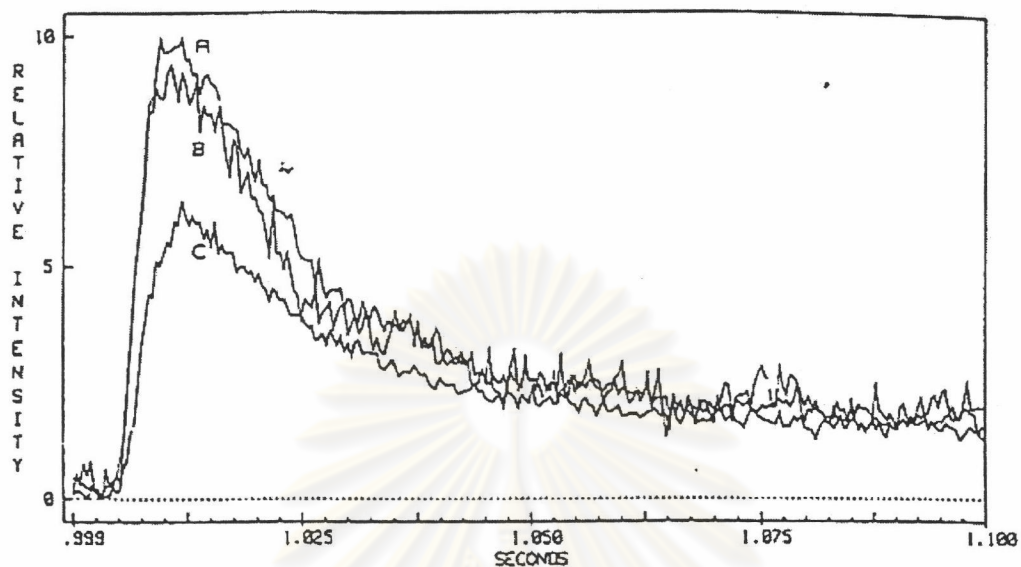


Figure 3.3 Comparison of C_3H_6/O_2 and C_3H_6 alone as reductants of NO: N_2 yield for (A) equilibrium C_3H_6/O_2-NO , (B) C_3H_6-NO (average of first 10 pulses), (C) C_3H_6-NO (after 50 pulses) [116]

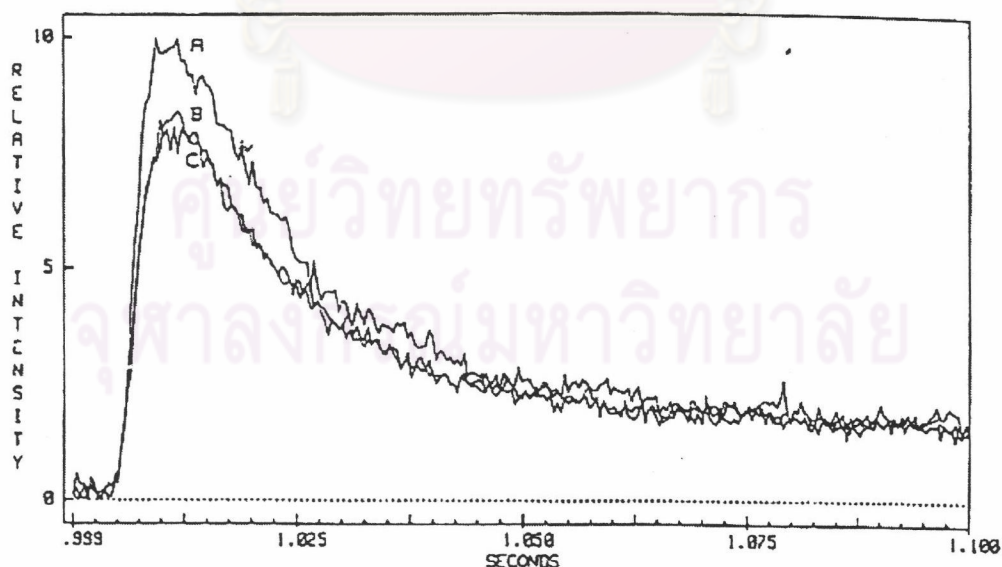


Figure 3.4 Comparison of C_3H_6/O_2 , CO and H_2 as reductants of NO: N_2 yield for (A) C_3H_6/O_2 , (B) CO, (C) H_2 [116]

It was significant to note that when C_3H_6/O_2 pulses were followed by NO pulses a small, but significant amount of CO_2 was observed. This suggested that even under net oxidizing conditions there was some tendency for carbonaceous species to become attached to the Pt. Possibly, therefore, under continuous flow conditions the lifetime of adsorbed propene species was quite long and sufficient to allow adsorption of NO at adjacent Pt sites.

The efficiency of CO or H_2 for NO reduction was completely eliminated when the excess oxygen was introduced. This was easy to understand on the basis that an individual CO and H_2 molecule had insufficient reducing power to remove adsorbed oxygen as fast as it was supplied by dissociative adsorption from the gas phase. Clearly, under these conditions the Pt remained in a more or less fully oxidized state and was totally inactive for NO reduction, producing instead NO_2 . On the other hand, the fact that the C_3H_6/O_2 pulses left the Pt in a state where a subsequent pulse of NO could be converted into N_2 showed that propene had sufficient reducing power to maintain some of the Pt in a reduced state even when the propene was mixed with an excess of oxygen.

The TAP results indicated that two mechanisms might operate together for NO reduction. The predominant mechanism comprising two basic steps is shown in Figure 3.5. The hydrocarbon reduces a patch of platinum atom from Pt-O to platinum metal and NO dissociation takes place on these reduced platinum sites. Once NO dissociation has begun there are two principal ways in which N adatoms can be removed dependent on temperature. At low temperatures, most of NO will be adsorbed molecularly, but only a fraction of it is dissociated. Therefore, the most likely means of nitrogen atom removal involves the reaction between adsorbed NO molecules and adsorbed N atoms to yield N_2O . However, at higher temperature where the concentration of N atoms is expected to be higher, the formation of N_2O is decreased because the most favored reaction becomes the recombination of two adsorbed N atoms to give molecular nitrogen. The small additional activity observed on fully reduced platinum when C_3H_6 is used as a reductant rather than CO or H_2 as shown in Figure 3.4 may be attributable to a second, less important, mechanism, in which NO dissociation is facilitated by reaction with adsorbed carbon-containing

species. For example, C_{ads} and NO_{ads} could combine to give NCO_{ads} or CNO_{ads} as intermediates on the way to the dissociation of NO_{ads} .

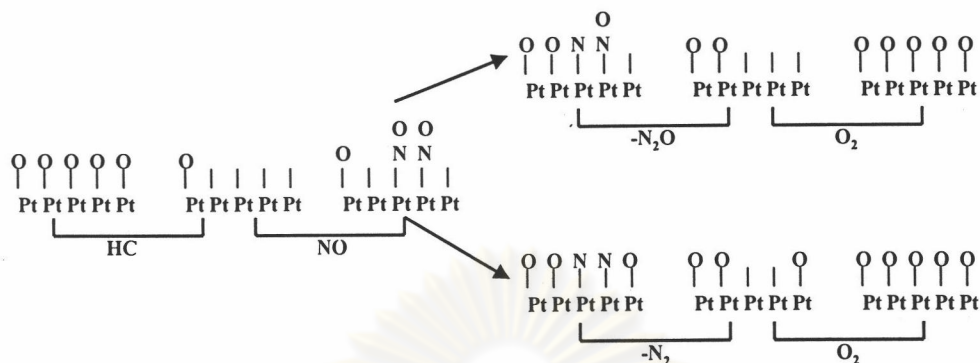


Figure 3.5 The NO decomposition mechanism for the selective catalytic reduction of NO by hydrocarbon on Pt-based catalysts under lean-burn condition [116]

The transient kinetic studies demonstrate that such a mechanism is feasible but, of course, can not prove that it is the correct mechanism, or the only mechanism, under real dynamic reaction conditions. To justify this model requires some evidence that NO decomposition, in competition with dissociative adsorption of O_2 can occur fast enough to account for the rates of N_2 formation observed experimentally [203]. A major problem in obtaining such information came from the fact that the Pt catalyst was self-poisoned by adsorbed oxygen so that a simply steady state NO decomposition experiment could not be undertaken. However, by making measurements of the extent of NO decomposition at short contact times and extrapolating back to zero time it was possible to get a good estimate of the minimum rate of this reaction. Alternatively, it should be possible to use a 'non-interfering' reductant, such as H_2 , to remove adsorbed O_{ads} so that the NO decomposition could continue to occur on reduced Pt sites. Table 3.1 compares the rate of NO decomposition at zero time with the rate of the NO/H_2 reaction and the rate of reduction of NO by C_3H_6 in the presence of a large excess of oxygen.

Table 3.1 A comparison of the rates of NO decomposition, the NO+H₂ reaction and the C₃H₆+NO+O₂ reaction on a Pt/Al₂O₃ catalyst at 240°C [203]

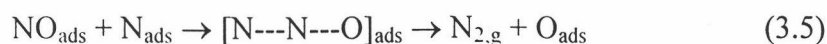
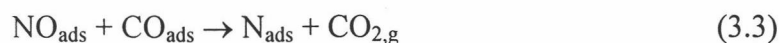
Reaction	TOF ($\times 10^{-2}/s$)	
	NO consumption ^a	NO decomposition ^b
C ₃ H ₆ +NO+O ₂	0.92	0.61
NO decomposition	4.21	4.21
NO+H ₂	45000 ^c	45000

^a Rate of NO consumption per exposed Pt atom.

^b Rate of NO decomposition per exposed Pt atom, calculated given that the decomposition of an NO molecule results in the formation of either 0.5N₂, NH₃ or N₂O.

^c By Arrhenius-type extrapolation from measurements at 30-65°C.

These results showed that the rate of NO decomposition on a reduced Pt surface was about seven times faster than the rate of NO reduction by C₃H₆. This meant that at steady state in the C₃H₆+NO+O₂ reaction ca. 14% of the Pt surface needed to be in a reduced state at any one time to sustain the NO decomposition reaction at the required rate. Hence, the rate of NO decomposition over reduced Pt was sufficiently fast under lean DeNO_x conditions to confirm the NO decomposition mechanism. However, since the decomposition of NO in the presence of H₂ was extremely fast, it seemed appropriate to suggest that under dynamic reaction conditions in the C₃H₆+NO+O₂ reaction an adsorbate-assisted dissociation of NO may take place. All that may be required for this was the presence on the surface of any adsorbed species, which had an affinity for oxygen. Likely candidates were H_{ads}, C_{ads}, CO_{ads}, C_xH_{y,ads} and possibly even another adsorbed nitrogen atom. As soon as a NO molecule adsorbed adjacent to such a species breaking of the N-O bond will be very rapid and the formation of N₂ can ensue. An adsorbate-assisted NO decomposition can be proposed by the following expressions:



After the proposal of the NO decomposition mechanism, many research works have reported to confirm this mechanism by using the other ways. An example was the results from the open literatures [124, 125] showing that neither the nitro and nitrito organic compounds nor isocyanate species were the most abundant species in $C_3H_6+NO+O_2$ reaction on Pt-ZSM-5 by using *in situ* diffuse reflectance infrared Fourier transform spectrometry (DRIFTS). Hence, the direct decomposition of NO seemed to be only possible way to produce nitrogen product.

The other example of the published paper [204] supporting the NO decomposition model proved the surface states of supported Pt catalysts by using a series of non-steady state transient switching experiments. It was found that the surface of silica supported Pt catalysts can be thought of as varying between two extremes during the $C_3H_6+NO+O_2$ reaction. First, the surface was predominantly carbon covered and reduced at low temperatures in a C_3H_6 containing atmosphere even though the gas mixture contained a very large excess of oxygen. C_3H_6 was adsorbed strongly and irreversibly on the surface. The carbon-covered surface could be oxidized at these temperatures by removing C_3H_6 from the gas phase. Conversely at higher temperatures the surface was predominantly oxidized. Removal of the O_2 from the reaction streams resulted in reduction and a build up of carbon on the surface while removal of C_3H_6 resulted in further oxidation of the surface relative to its steady state. The coverage of carbonaceous materials and O_{ads} species on Pt surface at different temperature suggested that at low temperatures the NO reacted by decomposition on reduced Pt sites, whereas at high temperatures it reacted with O_{ads} on oxidized Pt to form NO_2 .

3.2 NO Reduction Mechanism

On the basis of the NO reduction mechanism, it is a very complicated mechanism comprising many steps. However, there seem to be three important factors involving the activation of hydrocarbon, the activation of oxygen and the selective reduction of intermediates with NO_x in preference to oxygen. Focusing on the step of the formation of nitrogen containing products, the mechanisms proposed so far are divided into two major classes as follows:

1. The nitrogen containing products are formed by the reaction between the partially oxidized hydrocarbon compounds and the NO_x .

2. The nitrogen containing products are produced by the reaction between the nitrogen containing intermediate species and the O_2 or the NO_x .

It is realized that both classes occur through the interaction of two species, i.e., the intermediate species and the oxidizing agents. However, the difference of two classes is the presence or absence nitrogen atom in the intermediate species. It is remarked that NO_x may be in form either NO or NO_2 produced by NO oxidation.

Most evidences to confirm this reaction mechanism were obtained by *in situ* Fourier transform infrared spectroscopy, which could identify the intermediate species. Nevertheless, there were still many types of intermediate species proposed in the open literatures [121-123, 126-129]. Table 3.2 demonstrates some of the proposed intermediate species in the selective catalytic reduction of NO by hydrocarbons under lean-burn conditions over platinum group metal catalysts.

Table 3.2 The proposed intermediate species in the selective catalytic reduction of NO by hydrocarbons under lean-burn conditions over platinum group metal catalysts

The intermediate species	The oxidizing agents	References
- NO_2 (nitro)	NO_2, O_2	[121, 123]
- ONO (nitrite)	NO_2, O_2	[121]
- $\text{NO}^{\delta+}$ (nitrosonium)	$\text{NO}, \text{NO}_2, \text{O}_2$	[122]
- NCO (isocyanate)	$\text{NO}, \text{NO}_2, \text{O}_2$	[122, 123, 126]
- CN (cyanide)	$\text{NO}, \text{NO}_2, \text{O}_2$	[126, 127]
- CO (carbonyl)	NO_2, O_2	[121]
$\text{C}_x\text{H}_y\text{O}_z$	$\text{NO}, \text{NO}_2, \text{O}_2$	[128, 129]

The NO reduction mechanism models are also enclosed with the specification of the intermediate species. Subsequently, some models accompanying the detailed information are reviewed.

The detailed FT-IR studies on silica-supported Pt catalysts were performed in an attempt to obtain information in support of the proposal that organo-nitro and organo-nitrite surface species were involved as intermediates in the selective catalytic reduction of NO by propene in excess oxygen [121]. The reactivities of organo-nitro, organo-nitrite and organic carbonyl species examined by combining FTIR and gas phase analysis indicated that these species could react rapidly with NO₂ and O₂ to give N₂, N₂O and CO₂, but they were inactive to C₃H₆ and NO. From these results, the reaction mechanism is explained in Figure 3.6. It was concluded that C₃H₆ initially reacted with NO₂, which was formed from NO, resulting in the formation of nitro and nitrite species, where oxidation of NO to NO₂ was accelerated by platinum. Then the nitro and nitrite species were partly changed to carbonyl species at elevated temperatures and N₂ and N₂O as well as CO₂ were formed mainly from the reaction between NO₂ and carbonyl species and the reaction between O₂ and the N-containing species. In addition, the reactivity of model compounds was investigated and compared with the rate of NO reduction by C₃H₆ on the same catalysts in order to confirm the above hypothesis. It was found that oxidation of nitromethane and of n-butyl nitrite gave products similar to that obtained in the C₃H₆+NO+O₂ reaction as far as the N-containing inorganic compounds was concerned. Finally, it was noted that although isocyanate species had been invoked in the other literatures [122, 123, 126], no evidence for infrared bands due to isocyanate species was found in their work.

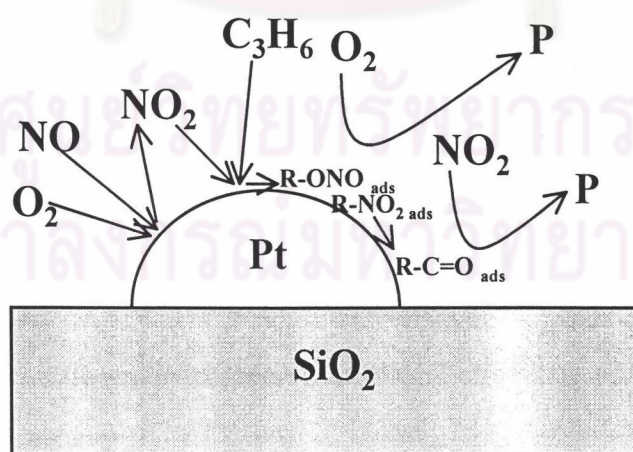
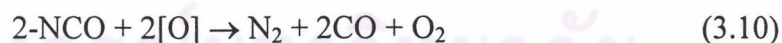
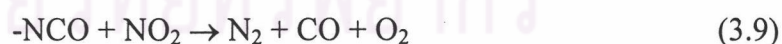
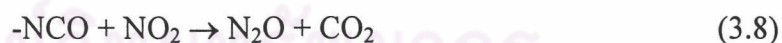


Figure 3.6 A proposed reaction scheme for the selective catalytic reduction of NO in the presence of excess oxygen over Pt/SiO₂ in case of nitro, nitrite and carbonyl species assigned as the intermediate species [121]

Under the *in situ* FT-IR studies of $C_3H_6+NO+O_2$ reaction over alumina supported platinum group metal catalysts, especially Rh/Al₂O₃ catalyst, the main surface species detectable by this technique were carbonate, adsorbed CO, nitrosonium, cyanide, isocyanate, adsorbed CO₂ and adsorbed hydrocarbon species as reported by the previous work [122]. However, only IR intensities due to nitrosonium and isocyanate bands were found to be strongly correlated to the activity for NO conversion and slightly related to the selectivity to N₂. Hence, it was suggested that both species might be possible candidates for either precursors or reaction intermediates in NO reduction scheme. On the basis of these results, a possible mechanism was that propene or its dehydrogenated analog, e.g., allylic species, adsorbed onto a support like alumina, interacted with oxygen species to form an oxygenated organic complex of the form C_xH_yO_z. Such a precursor could interact either with NO_x adsorbed on the edge of metal atom or with adsorbed and/or gas phase oxygen. In the former case an excited intermediate was formed which then fragmented into products such as cyanides and isocyanate species, etc.; and in the latter case further oxidation led to the formation of CO, CO₂ and H₂O. Subsequently, the -NCO might couple with adsorbed NO, NO₂ or O₂ to form a complex which after rearrangement decomposed into N₂, N₂O, CO, CO₂ and O₂ via reactions (3.6) to (3.10).



The reaction mechanism scheme about the proposal that organic nitro and isocyanate species are the intermediate species as found in the earlier work [123] is shown in Figure 3.7. First, C₃H₆ reacted with NO₂, which was formed from NO and O₂, resulting in the formation of organic nitro species. While, the isocyanate species formed at higher temperature was still unclear in their work. However, it was concluded that the main reactions for formation of N₂ and N₂O were those between

organic nitro species and NO_2 and/or O_2 at low temperature conditions and between isocyanate species and NO_2 and/or O_2 at high temperature conditions.

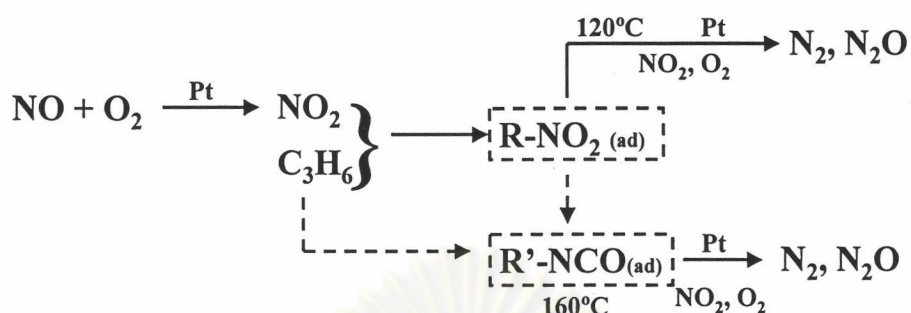
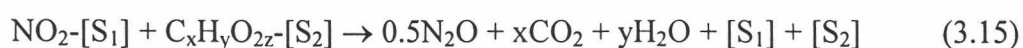
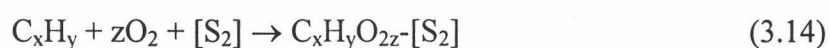
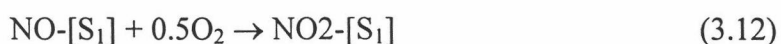


Figure 3.7 A proposed reaction scheme for the selective catalytic reduction of NO in the presence of excess oxygen over Pt/SiO₂ in case of nitro and isocyanate species assigned as the intermediate species [123]

An example of some published paper [135] proposed that partially oxidized hydrocarbon is devoted as the intermediate species is briefly mentioned. Using the DRIFT experiment on a platinum-based catalyst, it was concluded from the observation of a strong band at 1787 cm^{-1} assigned as a linearly adsorbed NO on platinum that the adsorption of NO on Pt sites was the first crucial step for the reduction of NO in the exhaust stream. By consideration of the initial product selectivity as a function of space velocity coupled with the spectroscopic characterization data could be interpreted that NO_2 and N_2 were most probably primary products of the reaction whereas N_2O was most probably a secondary product. The 'dual site' mechanism is schematized in Figure 3.8 and expressed by the following sequence of elementary steps:



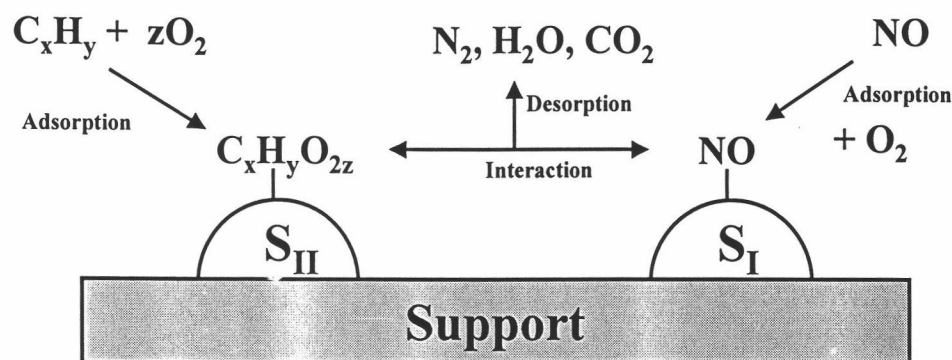


Figure 3.8 Proposed 'dual site' reaction mechanism for NO_x reduction in lean diesel exhaust gas on precious metal containing catalysts [135]

Although the specification of surface species towards *in situ* Fourier transform infrared spectroscopy has extensively been reported, there are still the other techniques in the proposal of NO reduction mechanism. An example of this case is the method involving temperature programmed reaction and transient studies using the temporal analysis of products (TAP) reactor having been performed to elucidate the reaction mechanism in the selective catalytic reduction of NO by C_3H_6 and C_3H_8 under excess oxygen over a Pt-ZSM-5 catalyst [128]. The observation that H-ZSM-5 was inactive for NO reduction at given conditions meant that all reactions were associated with only platinum sites. Under excess oxygen, the carbon-containing species were formed on the catalyst surface from C_3H_6 , but not produced from C_3H_8 , and the yields of N_2 and N_2O formed in the NO pulse were by far higher with C_3H_6 than with C_3H_8 . Therefore, it was suggested that the far higher NO conversions obtained with C_3H_6 in excess oxygen were due to the presence of propene-derived adsorbates on the surface and their chemical interaction with NO leading to N_2 , N_2O and CO_2 . Also, it was believed that NO decomposition on reduced platinum sites occurred only to a minor extent because if NO decomposition was the predominant mechanistic pathway, a similar efficiency of C_3H_6 and C_3H_8 for NO reduction should be anticipated, since the ability of both reagents to remove oxygen from the surface was shown to be very similar. The proposed main reaction pathway could thus be described as follows:

1. C_3H_6 reacted with adsorbed oxygen atoms (and, possibly, gas-phase oxygen) to CO_2 and adsorbed species of unknown composition, denoted as ' $C_xH_y(O_z)$ '.
2. NO could adsorb either on Pt-O sites, thus forming adsorbed NO_2 , or, possibly, on some bare Pt sites near the adsorbed hydrocarbon species.
3. The adsorbed intermediates, $C_xH_y(O_z)$, could react either non-selectively with oxygen to CO_2 or selectively with at least two NO_x molecules (either NO or adsorbed NO_2) to N_2 , N_2O and CO_2 .

5.3 Comment on Previous Works

As described in the literature reviews on the chapter II and chapter III, the case of the noble metal catalysts used in the selective catalytic reduction of NO by hydrocarbons under lean-burn conditions has proved very challenging, not least because the realization that these catalysts are very active for the reaction strongly oxidizing conditions and with high space velocities is not immediate. A high activity is generally observed at low temperatures, but with too narrow a range. For most examples, the efficiency is only very little affected by the presence of water, while it is also known that noble metals show some resistance to sulfur dioxide poisoning.

Attempt to elucidate the influencing parameters is taken close to consideration in detail in order to seek a way to overcome the obstacle about limitation of these catalysts. Among various noble metals, Pt is found to be the best catalyst under lean-burn conditions due to its high activity at low temperature. However, the crucial problem is still a large production of nitrous oxide. The selection of appropriate reductants may assist to enhance the catalytic performance but it is difficult for the application in practice. The possible three ways for improvement the catalytic performance are currently suggested from the consideration in the obtained available information.

The observation of an upper limit in capacity of monometallic Pt catalyst to selectively reduce NO at any temperature results in the challenge to find ways of promoting the Pt to obtain a conversion above this limit. The observation of an essential effect in the change of the platinum particle size and the nature of support as

well as platinum precursor results in the development of procedure in the catalyst preparation to change the catalytic properties leading to a better catalytic activity. The observation of the kinetic information results in the introduction of additional hydrocarbon to prevent the combustion with O_2 and be selective the reduction of NO.

Although the promising development has continuously reported, it remains important to understand the reaction mechanisms in order to give a judicious choice for the second metal, the controlling preparation and the style of the hydrocarbon addition. However, the proposal about the reaction mechanism, viz., NO decomposition and NO reduction mechanism, is still in argument. Each research group independently claims own results to support the speculated reaction models. Most characterizations emphasize to the use of infrared technique and transient method. Hence, a new aspect about the investigation of surface species through temperature programmed technique is practically offered to confirm the reaction mechanism.



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