CHAPTER III
THEORY

The selective catalytic reduction (SCR) of NO_x with ammonia by V_2O_5/TiO_2 catalyst has been extensively employed in industrial process for controlling the pollution due to nitrogen oxide gases from stationary source. In this chapter, an attempt is made to describe the SCR of NO_x by NH_3 reaction and the by-reaction, molecular structure of titanium oxide supported vanadium oxide catalysts, adsorption and desorption studies on V_2O_5 - based catalysts, and proposed intermediate species, reaction schemes and reaction mechanisms for the SCR of NO_x by NH_3.

3.1 The SCR of NO_x by NH_3 reaction and the by-reaction [Heck & Farrauto 1995]

The acid rains and town smog, produced mainly by atmospheric pollutants like SO_x, NO_x and volatile organic compounds are among the most serious world ecological problems. In the case of nitrogen oxide emissions, most of NO_x are produced during the combustion processes (thermal NO_x) by the oxidation of the atmospheric nitrogen at very high temperatures. NO_x typically consists of a mixture of 95% NO and 5% NO_2. Other NO_x are formed by oxidation of the organic nitrogen present in the fuel (fuel NO_x) and HCN formed from fuel nitrogen (prompt NO_x). [Hall & Bartok (1971), Bosch & Janssen (1988)]
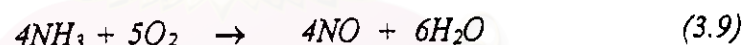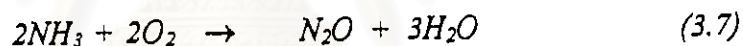
$$N_2 \;+\; O_2 \quad\rightarrow\quad 2NO \qquad (3.1)$$
$$NO \;+\; 1/2\,O_2 \quad\rightarrow\quad NO_2 \qquad (3.2)$$

SCR of NO_x using NH_3 was first discovered in 1957. It is discovered that NH_3 can react selectively with NO_x, producing elemental N_2. The major desired reactions are:

$$4NH_3 \;+\; 4NO \;+\; O_2 \quad\rightarrow\quad 4N_2 \;+\; 6H_2O \qquad (3.3)$$
$$4NH_3 \;+\; 2NO_2 \;+\; O_2 \quad\rightarrow\quad 2N_2 \;+\; 6H_2O \qquad (3.4)$$

The reaction between NO and ammonia can also proceed in a different way, giving rise to the undesired product N_2O:

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (3.5)$$
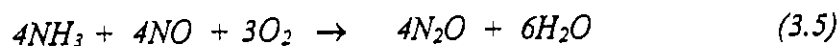
In general, under typical SCR conditions, with NH_3/NO near 1, few percent oxygen and $T < 400^{\circ}C$, [Bosch & Janssen (1988)] reaction (3.3) accounts for the overall stoichiometry on the best catalysts. Accordingly, the SCR process occurs when N_2 is produced with selectivity close to 100% and the ratio of converted moles of NO and NH_3 is 1. Unselective behavior occurs when products other than N_2 (namely N_2O) are formed (e.g. via reaction (3.6)) and/or when the ratio of converted NO and NH_3 moles is lower than 1. This implies that ammonia is converted by ways other than reaction (3.3), i.e. is in part oxidized by oxygen instead of NO through one of the following ways:

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (3.7)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (3.8)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (3.9)$$

Reactions (3.7) - (3.9) are the so-called SCO process (selective catalytic oxidation of ammonia). Several active SCR catalysts are also active in SCO although at slightly higher temperatures. For the temperature below about $100-200^{\circ}C$, the ammonia can also react with the NO_x present in the process gas producing explosive NH_4NO_3:

$$2NH_3 + 2NO_2 + H_2O \rightarrow NH_4NO_2 + NH_4NO_3 \qquad (3.10)$$
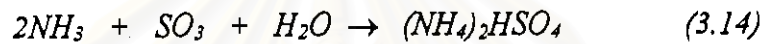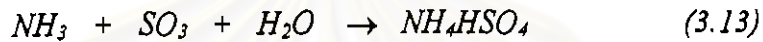
When sulphur is present in the flue gas, such as in coal-fired boilers or power plants, in petroleum-derived liquid fuels such as distillate or diesel, the oxidation of SO_2 to SO_3 (equations (3.11), (3.12)) results in formation of H_2SO_4 upon reaction

with H_2O.   Obviously, this results in condensation downstream and excessive corrosion of process equipment.

$$2SO_2 \; + \; O_2 \; \rightarrow \; 2SO_3 \qquad\qquad (3.11)$$

$$SO_3 \; + \; H_2O \; \rightarrow \; H_2SO_4 \qquad\qquad (3.12)$$
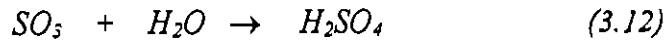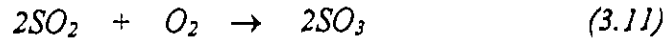
The reaction of NH_3 with SO_3 also results in formation of NH_4HSO_4 and/or $(NH_4)_2HSO_4$ (equations (3.13), (3.14)), which deposits on downstream process equipment such as heat exchanger and causes a loss in thermal efficiencies.

$$NH_3 \; + \; SO_3 \; + \; H_2O \; \rightarrow \; NH_4HSO_4 \qquad\qquad (3.13)$$

$$2NH_3 \; + \; SO_3 \; + \; H_2O \; \rightarrow \; (NH_4)_2HSO_4 \qquad\qquad (3.14)$$

3.2 Molecular structure of titanium oxide supported vanadium oxide catalysts

V_2O_5/TiO_2 is one of the best catalysts for reduction of nitric oxide with ammonia, an important process for minimizing NO_x emission from exhaust gases from power plant. This catalyst can operate best in a temperature range between 200 and 450°C. The structure of the surface vanadium oxide phase in supported vanadium oxide catalysts depends on both the particular gas and solid environment. [Haber *et al.* (1997)] Under ambient conditions, the structure of the surface vanadium oxide is controlled by the net surface pH of the surface layer. [Deo & Wachs (1991), (1994)] Figure 3.1 shows the possible structure of VO_x species.
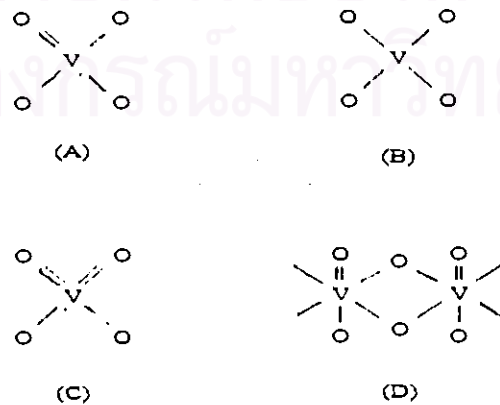

Figure 3.1: Possible structure of VO_x species [Bond & Tahir (1991)]

Calcination temperature and additives affect the net surface pH of the surface layer. Higher calcination temperature results in a decrease of the surface area of the oxide support, which increases the effective vanadium oxide loading per unit surface area and consequently, decreases the net surface pH of the surface layer. [Deo & Wachs (1994)] Regarding additives (including impurities and promoters), it can be divided into 2 types. Noninteracting additives, they are defined as surface metal oxides that preferentially coordinate with the oxide support rather than the surface vanadia species under dehydreated condition. Typical noninteracting additives are surface oxides of W, Nb, S, Si, Mo, Ni, Co and Fe. Consequently, the noninteracting additives can only indirectly affect the molecular structure of the surface vanadia species via lateral interactions. These additives posses a low surface pH, decrease the net surface pH of the surface layer. Another type, interacting additives is defined as surface metal oxides that preferentially coordinate with the surface vanadia species rather than the oxide support under dehydreated condition. Typical interacting additives are P and alkali/alkali earth oxides (K, Na, Ca, etc.) that tend to complex with the acidic surface vanadia species. These additives posses a high surface pH, increase the net surface pH of the surface layer. The basic alkali/alkali earth additives do not change the trigonal-pyramidal coordination of the dehydrated surface vanadia species, but do affect the V-O bond lengths by significantly increasing the terminal V=O bond length and consequently, decreasing the bridging V-O bond lengths. Thus, interacting additives can both modify the local structure of the surface vanadia species, affecting the V-O bond lengths, as well as form crystalline mixed metal oxide phases because of their chemical affinity for vanadia. [Wachs &Weckhuysen (1997)]

The specific structure or modification of the oxide support has influence upon the molecular structure of the dehydrated surface vanadia species. Titanium oxide (TiO_2) occurs naturally in three crystalline forms: anatase, rutile, and brookite. The last is not common. Catalytically, the anatase form is the most important in that it has the highest surface area (50-80 m^2/g), and is thermally stable up to about 500°C. The rutile structure has a low surface area (<10 m^2/g), and can form from anatase at about 550°C, resulting in occlusion of the vanadia and, ultimately, deactivation. The surface vanadia phase possesses a different structure on TiO_2 (anatase) and TiO_2 (rutile). [Deo

et al. (1992)] Possibly, the structure of V_2O_5 which form on anatase support having the crystallographic matching, but not on rutile because of the absence of a crystallographic fit. [Wachs & Weckhuysen (1997)] In addition, the specific preparation method had essentially no effect on the structure of the surface vanadia species. [Bond (1997)]

## 3.3 Adsorption and desorption studies on V_2O_5-based catalysts

Generally, in catalysts, the different species can form on the catalyst surface, that are potentially active in the SCR reaction. Adsorption and desorption studies are the methods to obtain knowledge about concerning the nature of the active species (*e.g.* NH_4^+ vs. coordinated NH_3, gaseous NO vs. adsorbed NO species), the reaction intermediates involved in the reaction, as well as on the nature of the actual catalyst active sites (*e.g.* V=O sites vs. V-OH sites). These methods have been extensively applied since the 1970s.

3.3.1 NH_3 adsorption and desorption

TPD, FTIR and combined TPD-FTIR are used to investigate the adsorption-desorption characteristics of ammonia on V_2O_5-based catalysts. Ammonia adsorbs on pure V_2O_5, on V_2O_5/TiO_2, on V_2O_5-SiO_2 /TiO_2, V_2O_5-WO_3 /TiO_2, V_2O_5-MoO_3 /TiO_2 in two different strongly held species; (i) molecularly adsorbed ammonia, through a Lewis-type interaction on coordinatively unsaturated cations and (ii) ammonia adsorbed as ammonium ions, over Brønsted acidic −OH surface hydroxy groups. Other species, like H-bonded NH_3 on oxide sites through one of its own hydrogen atoms [Lietti *et al.* (1993)] is certainly weakly held, so that it is not supposed to be active in the SCR process.

Pure TiO_2- anatase supports show Lewis acidity [Ramis *et al.* (1990)], whereas ammonium ions are formed on V-OH sites. The vanadyl sites are Lewis acidic that can convert into Brønsted sites by water adsorption (figure 3.2). Figure 3.3 shows structures for ammonia adsorbed on V_2O_5/TiO_2.

In the case of V_2O_5-WO_3 /TiO_2 and on V_2O_5-MoO_3 /TiO_2, like on WO_3 /TiO_2 and on MoO_3 /TiO_2 [Lietti *et al.* (1996b)], Lewis bonded species on wolframyl or molybdenyl species and Brønsted-bonded NH_4^+ species at W-OH sites and Mo-OH are formed.
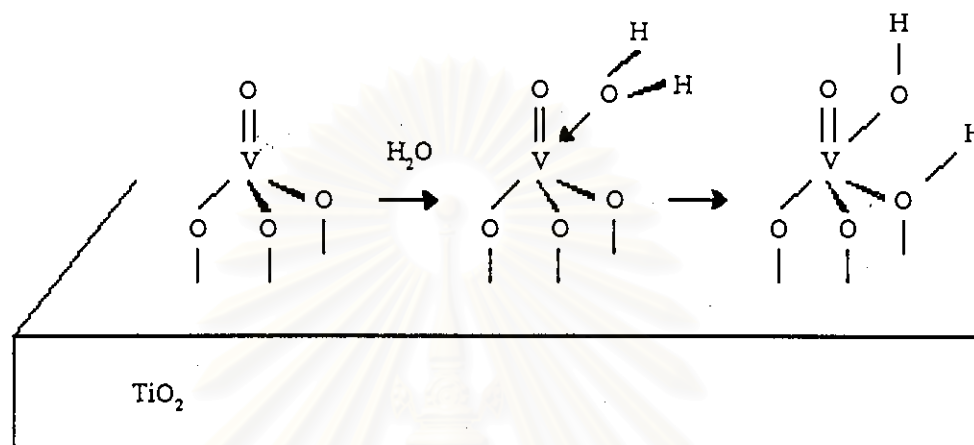
Figure 3.2: Schemes of the generation of the Brønsted acid sites from surface vanadyl centers [Busca *et al.* (1998)]
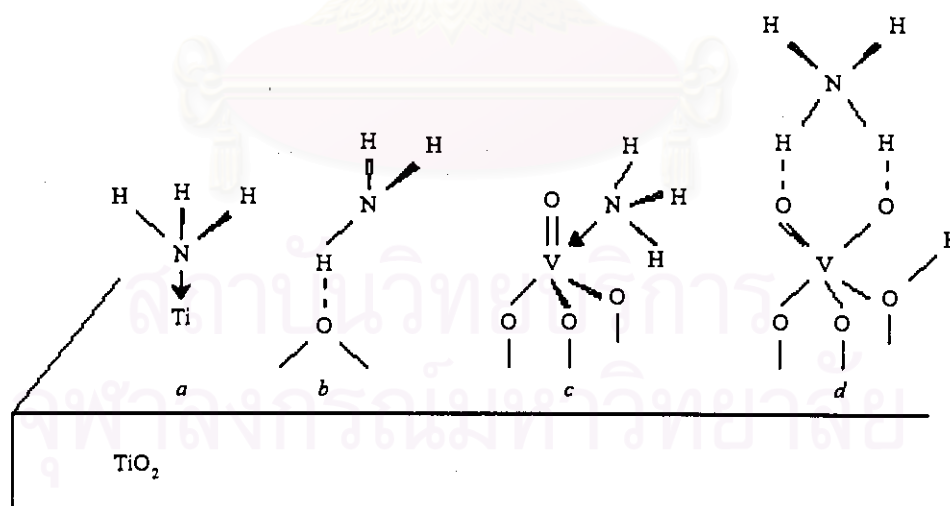
Figure 3.3: Proposed structure for ammonia adsorbed on V_2O_5/TiO_2; (a) Lewis-bonded NH_3 at Ti sites, (b) H-bonded NH_3 on oxide sites, (c) Lewis-bonded NH_3 at vanadyl sites, (d) ammonium ions bonded at V Brønsted acid sites [Busca *et al.* (1998)]

TPD method has showed that NH_3 strongly adsorbs on pure TiO_2, vanadia/titania and ammonia surface species having different thermal stability exist on the catalyst surface. The temperature typical of the SCR process is a significant part of ammonia adsorbed on the catalyst surface. In addition, both the amounts and the strength of adsorption decreases upon addition of V_2O_5, thus indicating that the V component decreases the catalyst surface acidity.

3.3.2 NO adsorption and desorption

In principle, NO can adsorb in a molecular forming, giving rise to surface nitrosyls where it interacts with a lone pair of the N atom to the surface metal cationic centers. And it can be oxidized by oxide surfaces, giving rise to species like nitrosonium ion (NO^+), nitrite ions (NO_2^-), adsorbed nitrogen dioxide (NO_2), nitronium ion (NO_2^+), and nitrate ions (NO_3^-). However, it can also act as an oxidizing agent reducing itself to NO^- and to its dimeric form, the hyponitrite anion ($N_2O_2^{2-}$), as well as to N_2O and N_2. Moreover, it can dimerize to dinitrogen dioxide N_2O_2 (which is possibly an intermediate in its reduction and/or in its oxidation) and to disproportionate giving rise to both reduced and oxidized species.

The interaction of NO on pure V_2O_5, on V_2O_5/TiO_2, on V_2O_5-SiO_2 /TiO_2, V_2O_5-WO_3 /TiO_2, V_2O_5-MoO_3 /TiO_2 is very weak. Upon contacting a V_2O_5/TiO_2 sample with NO, having the formation of a surface nitrosyl species, coordinated to Ti^{4+} sites. [Ramis et al. (1990)] In general, NO adsorbs as nitrosyl and dinitrosyl surface species on reduced vanadia surfaces, whereas it does not adsorb over fully oxidized surfaces. On the other hand, NO does not adsorb on an ammonia covered surface since NH_3 blocks the Ti^{4+} adsorption sites due to its greater basicity, and only a minor formation of nitrate species. Nitrate and/or nitrite species are formed slowly at room temperature and desorbed or decomposed easily.

3.3.3 NO + NH₃ co-adsorption and surface reaction studies on V₂O₅-based catalyst

The spectroscopic (*e.g.* FT-IR and Laser-Raman), surface reactivity techniques (*e.g.* temperature programmed reaction studies; TPD, TPR and TPSR) are used to study co-adsorption and surface reaction on V_2O_5-based catalyst. Using IR reactor cell is a method to detect the surface species (and possibly surface intermediates) while the reaction is occurring. The surface species could also be identified by these techniques present upon reaction (mass-spectrometry, FT-IR). [Ramis *et al.* (1990), Duffy & Curry-Hyde (1994b), Topsøe *et al.* (1995a, b), Lietti *et al.* (1996a, b, c)]

Regarding the co-adsorption of NH_3 with NO on V_2O_5/TiO_2 [Ramis *et al.* (1990)] and V_2O_5-WO_3/TiO_2 catalysts [Lietti *et al.* (1996b)], ammonia has been adsorbed on the surface of the catalysts and then the catalysts have been heated in the presence of NO. The reaction has been occurred involving the molecularly adsorbed ammonia species with NO, possibly via the amide species, leading to the formation of water and of N_2. In the same way, ammonia adsorbed on the Brønsted acid sites associated with V^{5+}-OH species is predominantly involved in the SCR reaction. The V=O sites are also involved in the activation of adsorbed ammonia and accordingly were found to play an important role in the catalytic cycle. No adsorbed NO species appears on the catalyst surface. That means the SCR reaction involves gaseous or weakly adsorbed NO. [Odenbrand *et al.* (1994), Topsøe *et al.* (1995a, b)]

For the investigation of mechanistic aspects of the SCR reaction over pure TiO_2, V_2O_5/TiO_2, WO_3/TiO_2, V_2O_5-WO_3/TiO_2 catalysts, the role of gaseous oxygen, NH_3 coverage, V and W loading on the SCR reaction is the factors of this studies. The catalyst redox properties are the key factors in controlling the reactivity of vanadia-based catalysts, and that the increase in the catalysts reactivity that is observed by either increasing the V and/or W loading is ascribable to the increased redox properties of the catalysts at low temperature. Similarly, the surface acidity is the important role in the adsorption and activation of ammonia at high temperature. [Lietti *et al.* (1996a, b,c)]

In addition, adsorption-desorption of the reactants (NH₃ and NO) on the catalysts can confirm that NO does not appreciably adsorb on the catalyst surface, wheareas ammonia is strongly adsorbed. The study of the dynamic of the SCR reaction shows that: (i) the reaction involves a strongly adsorbed ammonia species and gaseous or weakly held NO, (ii) the rate of the DeNO$_x$ reaction depends on the ammonia surface concentration for NH₃ coverage below a characteristic critical value, whereas a much weaker dependence, if any exists at high coverage. [Odriozola *et al.* (1991), Duffy *et al.* (1994b)]

However, a reservoir of adsorbed ammonia species available for the reaction is present on the catalyst surface. The ammonia storage is almost entirely consumed in the SCR reaction, is likely associated to Ti- and W-bound ammonia species, that are known to be strongly adsorbed on the catalyst surface but scarcely reactive in the SCR reaction. These species are likely involved in the SCR reaction upon migration (possibly in the gas phase, via desorption and re-adsorption) to near-by reactive V sites once these sites are available. Accordingly the Ti- and W-bonded adsorbed ammonia species (that represent the major fraction of adsorbed NH₃ over typical SCR catalysts) do not act simply as spectators in the SCR reaction but are involved in the NO consumption.

3.4 Proposed intermediate species, reaction schemes and reaction mechanism for the SCR of NO$_x$ by NH₃ [Busca *et al.* (1998)]

The mechanism of the SCR reaction and the nature of the species potentially active in it have been investigated over vanadia-based catalysts since the 1970s. Studies have been based on the results of reaction kinetics and of spectroscopic investigations of the adsorption of the reactants. The surface species that supposed to be involved in the most popular reaction schemes for SCR are summarized in table 3.1. Some proposed mechanism and intermediate on V₂O₅-based catalysts can used the difference in reactant species in order to divide into 7 groups:

Table 3.1: Proposed reactant species, intermediates and active sites in different mechanism and/or kinetic schemes for SCR on vanadia-based catalysts from many researchers [Busca *et al.* (1998)]

Reactant species		Intermediate	Catalyst	Supposed active site	Reference
From NH_3	From NO				
NH_4^+	O-N-O		V_2O_5		Takagi *et al.*
NH_4^+	NO gas	H-bonded complex	V_2O_5	$$\overset{\|\|}{-O-}\overset{}{V}\overset{}{-O-}\overset{\overset{OH}{\mid}}{V}\overset{}{-O}$$	Inomata *et al.*
$V-O-NH_2$	NO gas		V_2O_5/supp.	$O=V-O-V=O$	Janssen *et al.*
$V-ONH_4$	NO gas		V_2O_5		Ozkan *et al.*
$V-NH_2$	NO gas		V_2O_5		Ramis *et al.*
NH_3 ads.	N_2O ads.	$V-O^--H_3N-N=O-HO-V$	V_2O_5/supp.	$V=O$, V-OH	Maragonzis *et al.*
$V-O^--H_3N^+-HO-V$	NO gas		V_2O_5/TiO_2		Topsøe *et al.*

1. NH_4^+ from NH_3 and O-N-O from NO, the formation of two different sites denoted as $-O^-$ (which is the product of dissociation of a surface hydroxy group $-OH$) and $-O$, that in their mechanism is the same site with one electron less. However the proposed mechanism is electronically unbalanced (as well as site-unbalanced).

2. NH_4^+ from NH_3 and NO gas, this reaction consists in the reaction of ammonium ion species with gaseous NO, throughout an activated complex. The electronic structure of this intermediate and the interaction occurring have not been specified. Moreover, the movements of electrons upon the reactions have not been hypothesized. This mechanism is shown in figure 3.4.
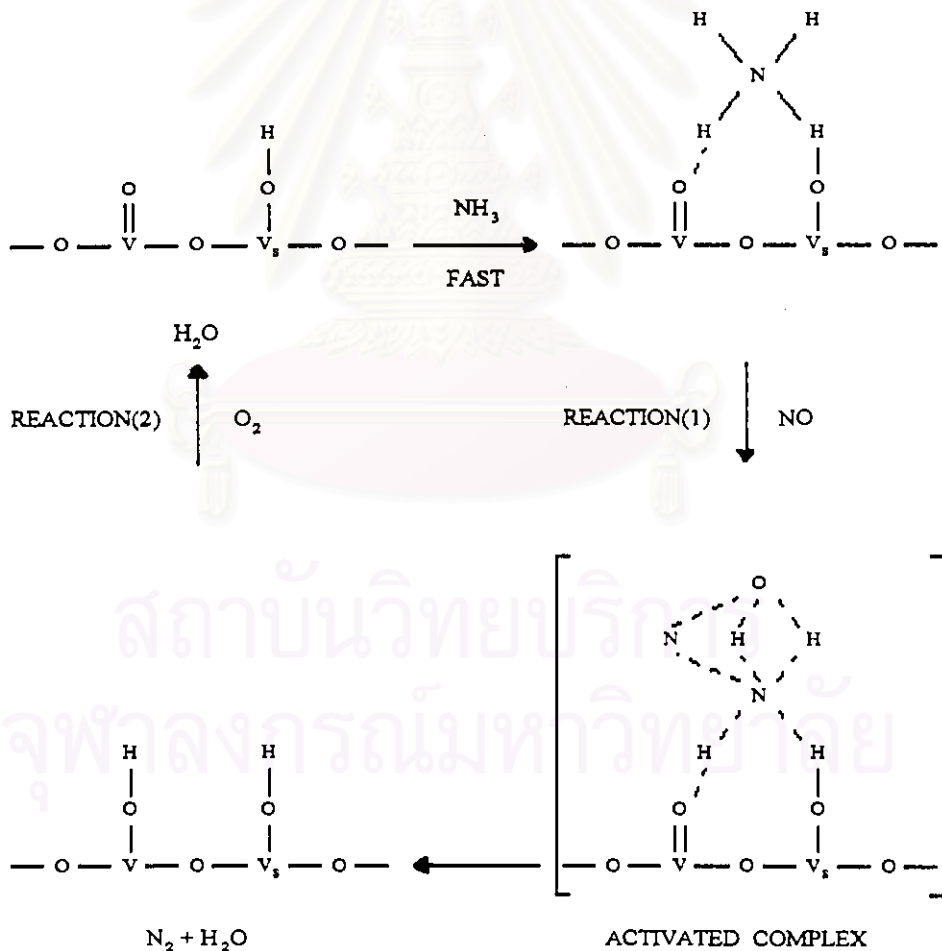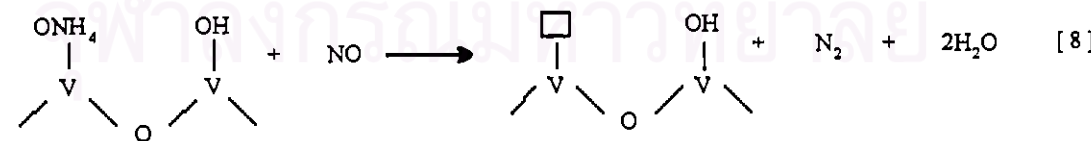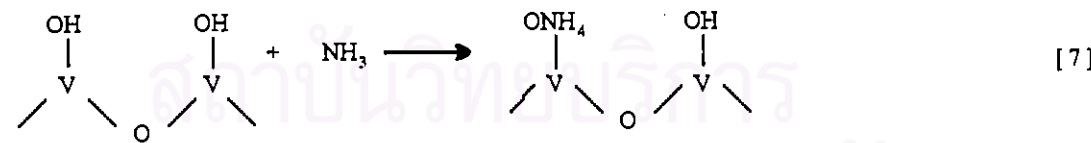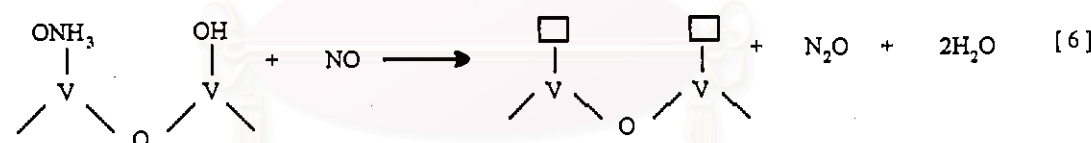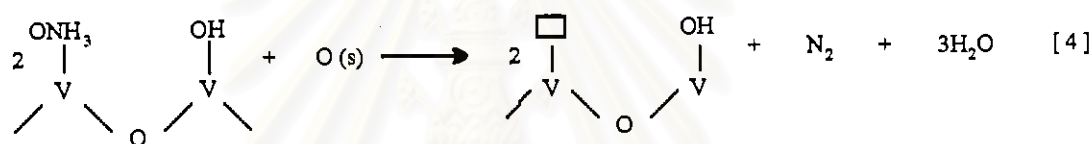

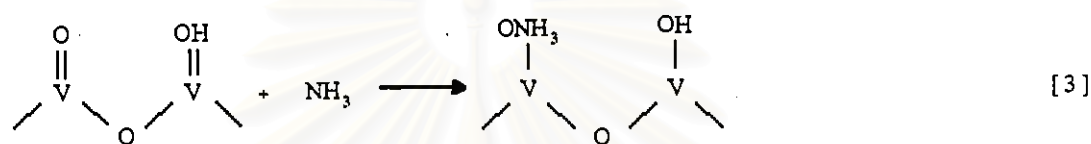
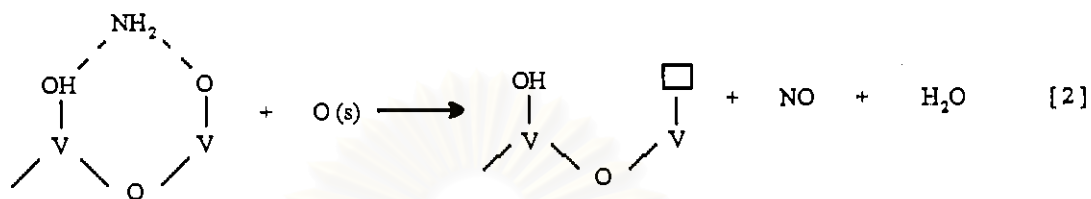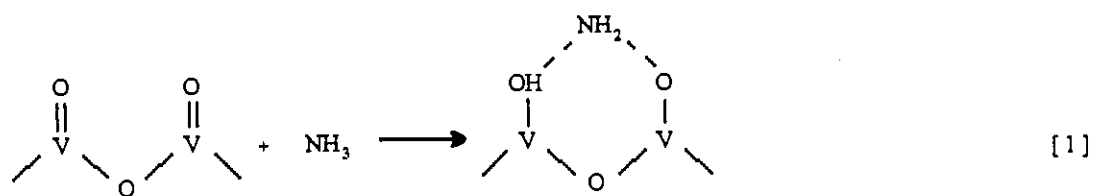**Figure 3.4:** Mechanism of the $NO-NH_3$ reaction on vanadium oxide catalysts proposed by Inomata *et al.* in the presence of oxygen [Busca *et al.* (1998)]

3. V-O-NH$_2$ from NH$_3$ and NO gas, in this case, adsorption of ammonia over polyvanadate species O=V-O-V=O leads to the intermediate species V-ONH$_2$ (species D of figure 3.5) that is proposed as the key intermediate in the SCR reaction. [Biermann & Janssen (1992), Ozkan *et al.* (1995)] This model is showed in figure 3.5. The formed species is formally a dissociated form of hydroxylamine (NH$_2$OH) which actually is a very weak acid. Metal complexes of hydroxylamine (through a coordination of the N atom lone pair to the metal) are known and can also be formed by hydroxylamine adsorption on metal oxide surfaces. Transition metal complexes of the NH$_2$O radical-like species have also been supposed to act as intermediates in hydroxylamine oxidation by such cations. Such an oxidation gives rise generally to N$_2$O or nitrates, but N$_2$ can also be obtained, depending on the cation and on its concentration.

4. V-ONH$_4$ from NH$_3$ and NO gas [Ozkan *et al.* (1995)], this species originates from NH$_3$+V-OH (step 7 of figure 3.6) and is thought to be involved in the SCR reaction with gas-phase NO (step 8). It is obvious that the formation of some of the above mentioned species from ammonia would cause the reduction of the adsorbing vanadium centers. Furthermore, a similar species to act as a precursor for NH$_3$ oxidation to NO (figure 3.6, steps 1+2) is proposed too. The other species to be formed from ammonia on vanadia-based catalysts (depicted as V-ONH$_3$) is produced by the reaction of V=O+NH$_3$. This species is supposed to be a precursor for N$_2$ and N$_2$O formation from ammonia (steps 3+4 and 3+5 of figure 3.6, respectively) or of N$_2$O from NH$_3$+NO (steps 3+6).
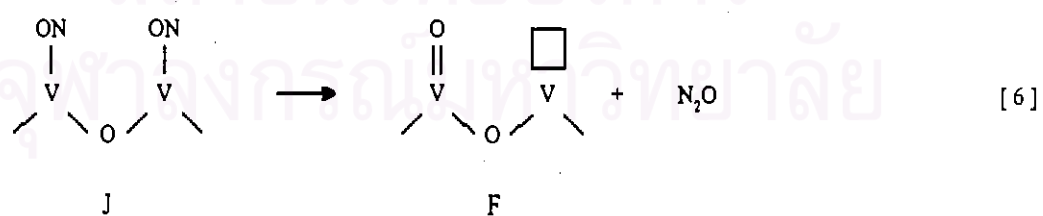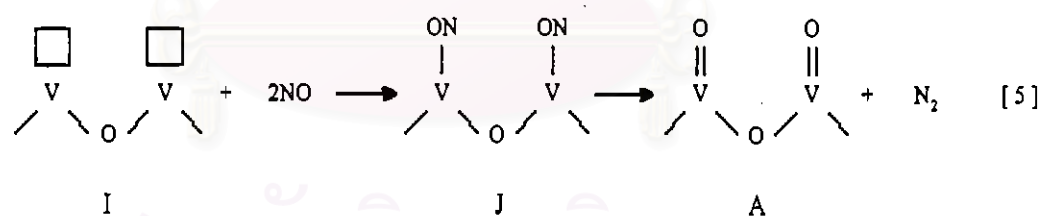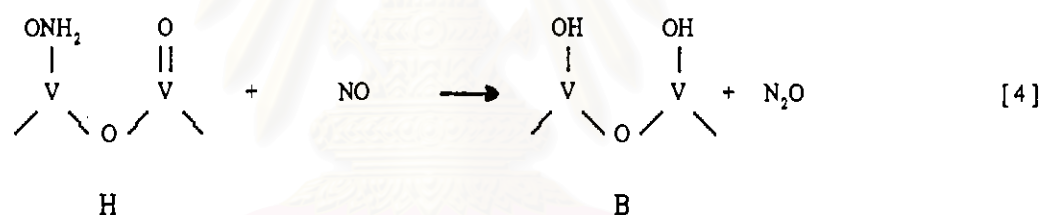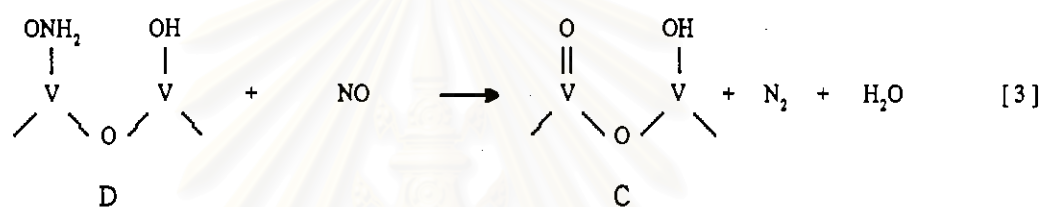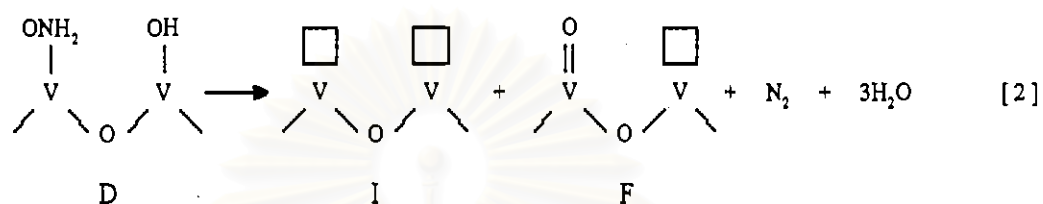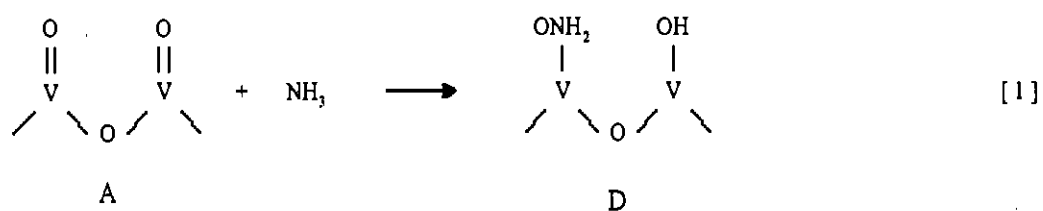
Figure 3.5: Mechanism of the NO-NH₃ reaction on supported vanadium oxide catalysts proposed by Janssen *et al.* in the presence of oxygen [Busca *et al.* (1998)]

Figure 3.6: Mechanism of the NO-NH$_3$ reaction on vanadium oxide catalysts proposed by Ozkan *et al.* in the presence of oxygen [Ozkan *et al.* (1995)]

5. V-NH$_2$ from NH$_3$ and NO gas from NO [Ramis *et al.* 1990], the reaction pathway shown in figure 3.7. This pathway was proposed also for Cu-based catalysts. This mechanism consists of the following steps:
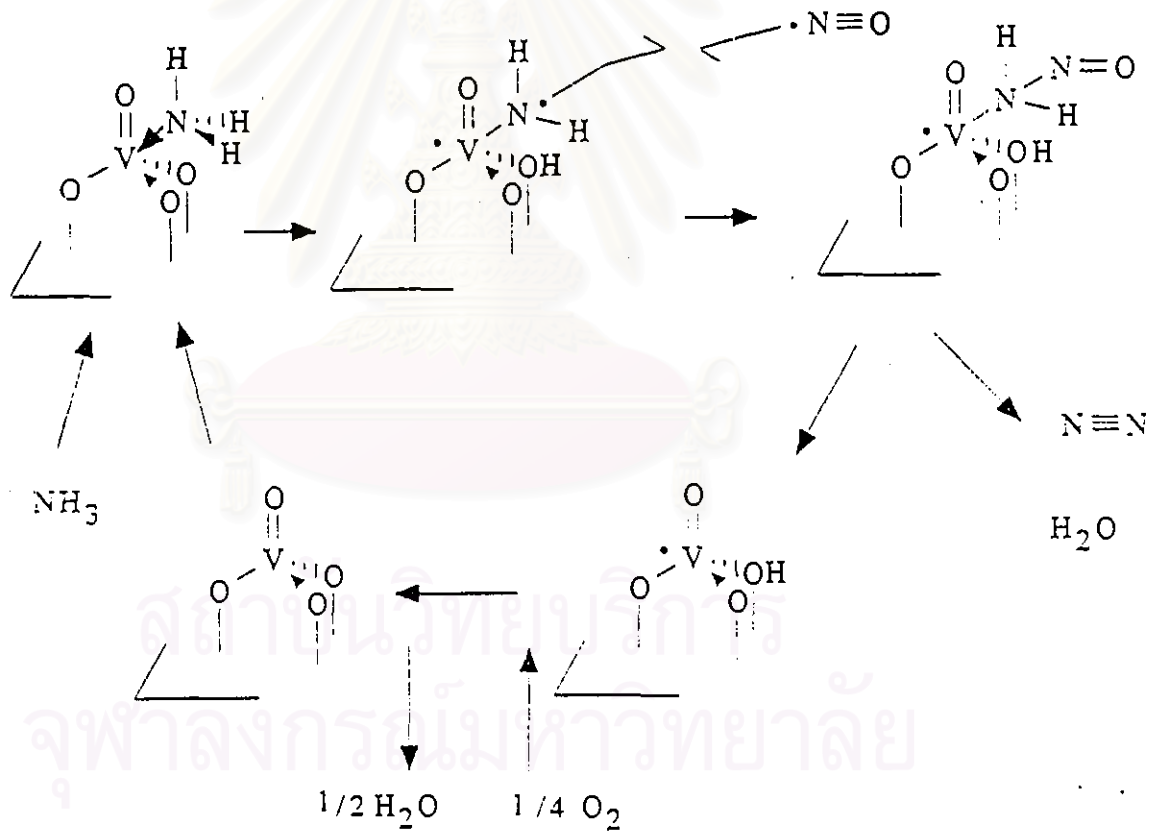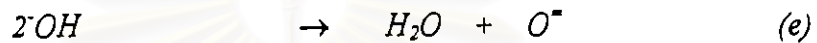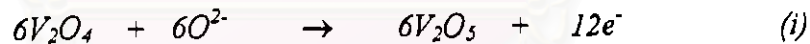
$$NH_3 + M^{n+} + O^- \rightarrow M^{(n-1)+}\text{-}NH_2 + {}^{\cdot}OH \quad (a)$$
$$M^{(n-1)+}\text{-}NH_2 + {}^{\cdot}OH \rightarrow M^{(n-1)+}\text{-}NH_2NO \quad (b)$$
$$M^{(n-1)+}\text{-}NH_2NO \rightarrow M^{(n-1)+} + N_2 + H_2O \quad (c)$$
$$M^{(n-1)+} + 1/2O_2 \rightarrow 2M^{n+} + O^- \quad (d)$$
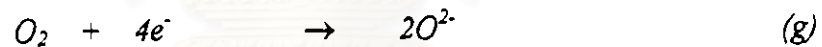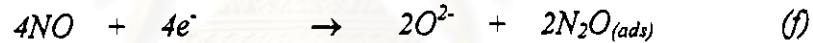$$2{}^{\cdot}OH \rightarrow H_2O + O^- \quad (e)$$

Figure 3.7: Mechanism of the NO-NH$_3$ reaction on supported vanadium oxide catalysts proposed by Ramis *et al.* in the presence of oxygen [Ramis *et al.* (1990)]

Accordingly, ammonia is adsorbed over a Lewis acid site that activates ammonia to an amide NH_2 species (step a), resulting in catalyst reduction. This activated ammonia species then reacts with gas-phase NO giving rise to a nitrosamide intermediate (step b), that then decomposes to nitrogen and water (step c). The reduced catalysts sites are then regenerated by gas phase oxygen (step d). The proper sum of these equations gives the reaction stiochiometry (equation 3.3). The key reaction step is supposed to involve a radical coupling between the $[M^{(n-1)+}\text{-}NH_2]$ surface species (whose amide moiety would act as a neutral radical), with the radical molecule NO. This is the first mechanism proposed for vanadia-base catalyst implying an activation of ammonia on Lewis acid sites.

6. NH_3 adsorption from NH_3 and N_2O adsorption from NO, in a kinetic study of the $DeNO_x$ SCR reaction over vanadium oxide catalysts, the proposed reaction mechanism is based on the following steps:

$$4NO \ + \ 4e^- \quad \rightarrow \quad 2O^{2-} \ + \ 2N_2O_{(ads)} \qquad (f)$$
$$O_2 \ + \ 4e^- \quad \rightarrow \quad 2O^{2-} \qquad (g)$$
$$6V_2O_5 + 2N_2O_{(ads)} + 4NH_{3(ads)} + 4e^- \quad \rightarrow \quad 6V_2O_4 + 4N_2 + 6H_2O + 2O^{2-} \ (h)$$
$$6V_2O_4 \ + \ 6O^{2-} \quad \rightarrow \quad 6V_2O_5 \ + \ 12e^- \qquad (i)$$

Steps (f) and (g) correspond to the chemisorption of NO and O_2, respectively: step (h) is the reaction of $N_2O_{(ads)}$ with $NH_{3(ads)}$ whereas step (i) is the catalyst reoxidation.

7. $V\text{-}O^-\text{-}H_3N^+\text{-}HO\text{-}V$ from NH_3 and NO gas from NO [Topsøe et al. 1995a, b)], the mechanistic scheme is shown in figure 3.8. In this mechanism, the catalytic activity relates to the ammonia adsorbed on the Brønsted acid sites associated with $V^{5+}\text{-}OH$ sites. $V^{5+}\text{=}OH$ groups are also involved in the reaction, and specifically in the activation of adsorbed ammonia. This activation process involves the transfer or partial transfer of hydrogen from the NH_3 molecule and accordingly reduced $V^{4+}\text{-}OH$ sites are produced. Once ammonia has been activated, NO from the gas-phase reacts with the activated ammonia complex leading to the formation of an intermediate that

then decomposes to nitrogen and water. Regeneration of the active sites (*i.e.* oxidation of the reduced V^{4+}-OH sites to V^{5+}=O groups) occurs by gas-phase oxygen. Accordingly, the proposed catalytic cycle consists of both acid-base and redox functions. In which the ammonia adsorption sites are considered to be Brønsted acid sites instead of Lewis acid sites.

DeNO$_X$ Catalytic Cycle
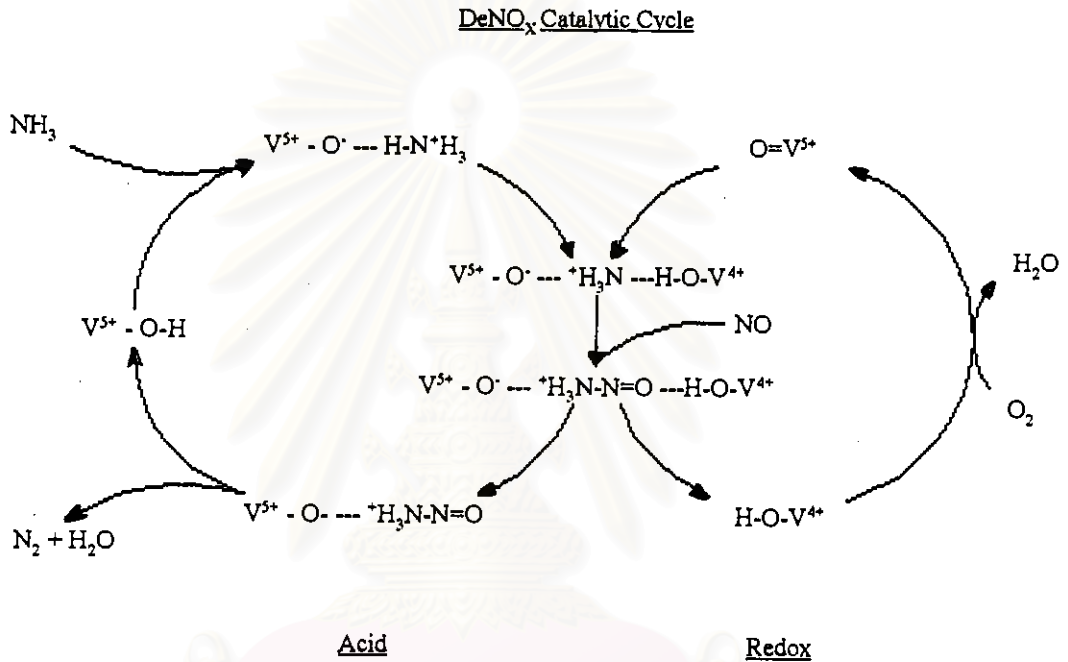
Figure 3.8: Scheme illustrating the catalytic cycle of the SCR reaction over vanadia/titania catalyst in the presence of oxygen proposed by Topsøe *et al.* [Topsøe *et al.* 1998]