CHAPTER II

LITERATURE REVIEWS

Control of NO_x emission from stationary sources has become an important application area for catalysis in recent year. The selective catalytic reduction by ammonia is still the most efficient process for the removal of NO_x from effluents of stationary combustion sources. It is generally accepted that the SCR process, NH_3 react selectively with NO_x, producing elemental N_2 and H_2O over a catalyst in excess amounts of oxygen. Among the various catalysts that have been used for the SCR, the supported vanadia-based catalysts still seem to be the most efficient. Although the numerous recent publications devoted to the mechanism and kinetics of the SCR process on the various supported vanadia-based catalysts for improving catalytic performance, there is as yet no common understanding of this problem.

2.1 Reviewed literature

There are many papers that concern with the supported vanadia-based catalysts in the SCR of NO_x with NH_3 as follows.
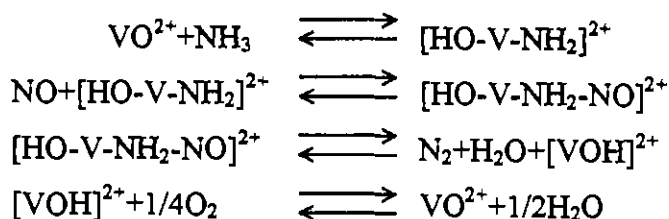
Tamaru and coworkers (1977) investigated the mechanism of the SCR reaction over vanadia-based catalyst suggested that the reaction proceeded via the two adsorbates NO_2 (ad) and NH_4^+(ad), which reacted through a Langmuir-Hinshelwood mechanism to form nitrogen and water.

Inomata et $al.$ (1980) argued that the oxidation of NO to NO_2 could easily take place at the conditions of Tamaru et $al.$ (1977) but could hardly occur under dilute gas conditions that were typical of the SCR process. Based on kinetic, spectroscopic and mechanistic information these authors proposed the mechanism: (i) ammonia was first strongly adsorbed as NH_4^+(ad) at a Brönsted acid site associated to V-OH and adjacent to V^{5+}=O; (ii) then gaseous NO reacted with NH_4^+(ad) according to an Eley-Rideal mechanism to form nitrogen, water and V-OH; (iii) V-OH species was

eventually reoxidized to $V^{5+}=O$ by gaseous oxygen. They postulated that $V=O$ assisted the activation of NH_3 and reported that the rate of the NH_3-NO reaction was proportional to the amount of $V=O$. This scheme has been confirmed and slightly modified by Janssen *et al.* (1986, 1987a-b) on the basis of experiments with labeled molecules: these authors proposed the $V=O$ species as the active centers for ammonia ($^{15}NH_3$) adsorption and activation to form-$O^{15}NH_2$ surface groups. This species then reacted with gaseous ^{14}NO via an Eley-Riedel type of mechanism leading to $^{15}N^{14}N$ and water. Formation of N_2O by-product was proposed to proceed via a dual-site mechanism involving the reaction of an adsorbed $-ONH_2$ surface species with a neighbor adsorbed $-NO$. In the case of high content V_2O_5/SiO_2-TiO_2 catalysts, where vanadia crystals were observed.

Oderbrand and coworker (1991) proved that the selectivity to N_2O was strongly reduced in the presence of water. This effect has been explained assuming hydration of the oxygen vacancies present in close proximity to a couple of vanadyl groups, which were envisaged by the authors as the active sites for the production of nitrous oxide.

Ramis *et al.* (1990) studied the adsorption of nitric oxide, nitrogen dioxide and ammonia and their coadsorption on vanadia-titania by FT-IR spectroscopy. Upon nitric oxide adsorption, a surface nitrosyl species was formed rapidly and nitrates were formed slowly by oxidation. Nitrogen dioxide adsorption formed nitrate species by oxidation and nitric oxide. Lewis-bonded molecular species and ammonium ions were formed upon ammonia adsorption. Coordinated ammonia was thermally more stable than ammonium ions and could lose a hydrogen atom to give an amide species. Adsorption on a water-covered sample showed that ammonia displaced water from Lewis sites. Experiments of nitric oxide adsorption on ammonia-covered vanadia-titania showed that ammonia poisons the nitric oxide adsorption sites and that NO_3^- species were formed by nitric oxide oxidation of vanadyl sites. By heating the ammonia-covered sample in the presence of gaseous nitric oxide coordinated ammonia reacted via the amide species, while ammonium ions did not. The following reaction mechanism was proposed:

$$VO^{2+}+NH_3 \rightleftharpoons [HO\text{-}V\text{-}NH_2]^{2+}$$

$$NO+[HO\text{-}V\text{-}NH_2]^{2+} \rightleftharpoons [HO\text{-}V\text{-}NH_2\text{-}NO]^{2+}$$

$$[HO\text{-}V\text{-}NH_2\text{-}NO]^{2+} \rightleftharpoons N_2+H_2O+[VOH]^{2+}$$

$$[VOH]^{2+}+1/4O_2 \rightleftharpoons VO^{2+}+1/2H_2O$$

This reaction sequence is believed to operate during the selective catalytic reduction of NO_x over vandia-titania based catalysts.

Chen and Yang (1992) studied the role of WO_3, on TiO_2-supported V_2O_5 and $V_2O_5+WO_3$ catalysts, over the commercial selective catalytic reduction catalysts. The activities of those catalysts were measured under both dynamic and steady state conditions. The catalysts were characterized by temperature-programmed reaction (TPR), ammonia chemisorption and proton magic angle spinning nuclear magnetic resonance (MAS NMR) measurements. The following effects of WO_3 on V_2O_5/TiO_2 in the commercial WO_3-V_2O_5/TiO_2 (co-impregnated) SCR catalysts were observed: (1) It increased the activity and widened the temperature windows for SCR. (2) It significantly increased the poison resistance to both alkali metal oxides and arsenious oxide. (3) It reduced ammonia oxidation (as well as SO_2 oxidation which was known from the published literature). Those results had been correlated directly with ammonia chemisorption and proton MAS NMR measurements. Those results suggested that the Brönsted acid sites were the active sites for the SCR. Addition of WO_3 in V_2O_5/TiO_2 increased the Brönsted acidity (both Brönsted acid site density and strength of the acid), whereas the alkali poison decreased the Brönsted acidity.

Weng and Lee (1993) examined the effect of Nb_2O_5 promoter on V_2O_5/TiO_2 catalysts for selective catalytic reduction of nitric oxide. Catalysts characterization was carried out by BET surface area measurement, temperature-programmed desorption, infrared spectroscopy and X-ray diffraction. A modified NO-NH_3 rectangular pulse (NARP) technique was introduced to measure the number of active sites and the acid sites increased with the content of Nb_2O_5 due to the increase in BET surface area. The Nb_2O_5 promoter in the lower and higher temperature ranges enhanced the activities of the SCR reaction and the ammonia oxidation, respectively.

Baltensperger and coworkers (1993) used positron emitting (NO)-N^{13} molecules produced with a cyclotron to investigate the selective catalytic reduction of NO by NH$_3$ over vanadia/titania at very low reactant concentrations. The (NO)-N^{13} concentration was on the order of 5×10^{-9} ppm, which was more than 11 orders of magnitude lower than the usually used concentrations. Catalyst samples were pretreated with NH$_3$ or H$_2$, without adding those reagents during the conversion experiments. Under those conditions the vanadia/titania catalyst pretreated with NH$_3$ kept its full activity for at least 5 hrs. At the low NO concentrations, 50% conversion could already achieve at 80 °C, with complete conversion at 150 °C. The reaction rate at 92 °C was 1.9×10^{-18} mole of NO (g of catalyst)$^{-1}$s^{-1}. That value was in good agreement with the value expected from measurements with a similarly prepared catalyst assuming a first order reaction in NO. The activation energy was calculated to be 37 kJ/mole, which compares fairly well with the one measured on a similarly prepared catalyst under usual reactant concentrations (43 kJ/mole). In contrast, vanadia/titania pretreated with H$_2$ did not show any NO conversion. Those results indicated that NH$_3$ was necessary for NO conversion and that one N atom of the formed N$_2$ originated from NH$_3$. Using a thermochromatographic apparatus, adsorption enthalpies (at zero coverage) for NO and NO$_2$ on various oxides were determined. Values of 21 ± 2 and 33 ± 3 kJ/mol were found for NO and NO$_2$, respectively, independent of the material.

Dumesic and coworkers (1993) investigated the selective catalytic reduction of nitric oxide with ammonia on vanadia/titania catalysts by microkinetic analysis. Based on fundamental information obtained from TPD/TPR and in situ FT-IR measurements, it had been possible to examine in detail the physical consistency of different reaction mechanisms. A simple, two-step Eley-Rideal mechanism with ammonia adsorption on a single site could not account for all the experiment observations. However, both the kinetic and spectroscopic information might be explained either by introducing in the mechanism two sites for ammonia adsorption or by including an activation step of the adsorbed ammonia.

Ozkan and coworkers (1993) studied the structural specificity of vanadium pentoxide catalysts in the selective catalytic reduction of nitric oxide. Catalysts were prepared by different temperature programmed methods to obtain particles having preferential exposure of different crystal planes. Catalyst samples were characterized using the BET surface area technique, X-ray diffraction, laser Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and 3-D imaging techniques. Samples that preferentially exposed the (010) basal planes were found to promote direct oxidation of ammonia more readily than nitric oxide reduction as evidenced by the differences in nitric oxide and ammonia conversions and nitrogen and nitrous oxide yields. The difference in catalytic activity and selectivity was related to the relative abundance of V=O sites exposed in the catalyst surface and the competing reactions that were involved in the SCR and direct ammonia oxidation reaction schemes.

The chemistry of the selective catalytic reduction of NO_X with ammonia over V_2O_5-TiO_2 and WO_3-TiO_2 catalysts had been investigated by Lietti and coworkers (1993a). They found that protonated and molecularly coordinated ammonia species, associated with Brönsted and Lewis acid sites respectively and with different thermal stability, were observed upon NH_3 adsorption. WO_3-TiO_2 showed stronger Lewis and Brönsted acid sites than V_2O_5-TiO_2. Upon heating in NO atmosphere, a reaction between adsorbed ammonia and gas-phase of weakly adsorbed NO was monitored by FT-IR and Temperature programmed surface reaction (TPSR) measurements. The results indicated that V_2O_5-TiO_2 was significantly more active than WO_3-TiO_2 due to its superior redox properties. Monomeric vanadyls and meta-vanadate polymers were proposed as the active sites in the active sites in the SCR reaction, the former sites showing lower reactivity. Oxygen was involved in the reaction and played a crucial role in determining the reactivity of the catalysts. Moreover, They also investigated the effect of K-doping on the surface and catalytic properties of sub-monolayer vanadia/titania catalysts (1993b) and suggested that isolated vanadyls and polymeric metavanadate species were present on the surface of undoped catalysts; both species increased on increasing the V_2O_5 loading in the range 0.28-5.3 %w/w. TPSR and TPR data provided evidence for a greater reactivity of polymeric metavanadate

species as compared to isolated vanadyls. Besides, a different type of isolated vanadyl appeared to form at high loading. Ammonia was adsorbed at vanadium sites in the form of molecularly coordinated species and of the ammonium ions. Coordinated species showed a higher thermal stability than ammonium ions. Ammonia was also coordinated at titanium sites to give a more weakly held species. Upon K-doping the stretching frequencies of surface vanadyls were lowered due to the production of strong oxide basic anions on the catalyst surface. That reduced the Lewis acidity of vanadium ions. IR and TPD experiments indicated that both molecularly chemisorbed ammonia and ammonium ions were present in much lower amounts and were less strongly held on K-doped samples. TPD and TPSR data further indicated that the alkali dopant poisons preferentially Lewis acid sites associated with vanadium rather than with Ti^{4+} ions. TPSR and TPR data showed that alkali doping reduced markedly the nitric oxide conversion (associated with the number of active sites). The lower number of active sites due to alkali addition, which resulted in a lower ammonia surface coverage.

Sazonova and coworkers (1994) reported the performance of V_2O_5-TiO_2 catalysts doped by WO_3 and Nb_2O_5 in sulfur dioxide oxidation, and in selective catalytic reduction of NO by ammonia. Addition of tungsten and niobium oxides was found to suppress sulfur dioxide oxidation thus increasing the catalyst resistance to SO_2 poisoning and their activity in SCR.

Schneider et al. (1994) examined selective catalytic reduction of NO by NH_3 on high surface area (BET>180 m^2g^{-1} vanadia-titania aerogels with 5, 10 and 20 wt% of vanadia. They concluded that the SCR activity of those catalysts increased with the vanadia loading. That behavior was reflected by the temperatures necessary to reach 50%NO conversion under standard conditions, which decreased in the sequence 5%V_2O_5, 272 °C; 10%V_2O_5, 197 °C; 20%V_2O_5, 167 °C. A similarly prepared high surface area (182 m^2g^{-1}) titania aerogel did not exhibit significant NO conversion in that temperature ranges. On pure titania aerogel, mainly Lewis-bound ammonia was observed subsequent to NH_3 adsorption at ambient temperature. In contrast, it its shown that Brönsted-bound ammonia, characterized by bands at 1660 and 1414 cm^{-1},

was involved in the SCR reaction. The SCR activities correlated with the fraction of Brönsted-bound ammonia that significantly increased with the vanadia loading of the aerogel samples.

Efstathiou and Fliatoura (1995) studied the kinetics of the selective catalytic reduction of nitric oxide with ammonia over an 8 mole%V_2O_5-TiO_2 catalyst in the temperature range 180-380 °C, nitric oxide and ammonia feed concentrations in the range 500-2500 ppm with excess of oxygen. It was found that the reaction order with respect to ammonia strongly depended on reaction temperature, in contrast to the case of the reaction order with respect to nitric oxide. The apparent activation energy of the reaction for nitrogen formation depended more on the feed concentration of ammonia peaks corresponding to desorption energies in the range 91.96-117.04 kJ. Transient isotopic experiments with ^{18}O, showed that at 400 °C only small amounts of lattice oxygen of V_2O_5 could be exchanged with gaseous oxygen. Similar experiments with (NO)-N^{15} showed also that only very small quantities of nitric oxide adsorbed on the catalyst surface from a mixture containing (NO)-N^{15}/O_2/He. The partial oxidation reaction of ammonia to nitrogen and nitrous oxide at 350 °C was studied by steady-state tracing techniques. The results obtained suggested that at the level of ammonia conversion of 75% there was an appreciable amount of NH_X intermediate species which were found in the reaction pathway of nitrogen formation, but a small amount was found on the reaction pathway of nitrous oxide formation. In addition, adsorption and desorption steps of ammonia must be considered as faster steps than those involved in reaction between adjacent adsorbed NH_X species to form nitrogen and nitrous oxide.

The influence of support on the activity of monolayer vanadia-titania catalysts in selective catalytic reduction of NO by ammonia had been carried out by Marshneva and coworkers (1995). The V_2O_5.TiO_2 catalysts were prepared via $VOCl_3$ grafting on the TiO_2 surface, V_2O_5.WO_3-TiO_2 catalysts were prepared by inserting ammonium salts in TiO_2. On the basis of catalytic activity data it might be concluded that the specific activity, activation energy, and turnover frequency did not depend on the crystal structure of titania. The activation energy of the selective catalytic reduction

process coincided with the vanadia reoxidation activation energy. Reoxidation of reduced vanadia species seemed to be the rate-limiting step of the SCR process. NO SCR by ammonia with and without oxygen might have a common reaction mechanism. Conversion of one $NO(NH_3)$ molecule proceeded on two surface vanadium atoms. Part of the supported vanadia penetrated into the sublayers of titania independent of the vanadia introduction method and titania crystal structure.

Alemany and coworkers (1995) characterized V_2O_5-WO_3/TiO_2 samples with compositions similar to those of commercial de-NO_X catalysts (WO_3 similar to 9% w/w, V_2O_5 < 3%w/w) by XRD, surface area and pore size distribution, Fourier transform infrared, laser Raman, UV-VIS diffuse reflectance, electron paramagnetic resonance spectroscopy, and catalytic tests in the reduction of NO_X by NH_3. The V_2O_5-WO_3/TiO_2 catalysts exhibited reactivity higher than the binary V_2O_5/TiO_2 and WO_3/TiO_2 samples with the same metal loading, and the temperature window for the SCR reaction was greatly widened. The catalysts consisted of anatase TiO_2 and their morphological properties closely resembled that of WO_3/TiO_2 for (V+W) surface coveraged lower than one. Monomeric vanadyls and wolframyls and polymeric W_wO_y groups were observed in the samples with low vanadia loadings that were apparently similar to those present on the surface of the binary oxide systems with comparable metal loadings. On increasing the vanadium loading, polyvanadate species were also formed. EPR, FT-IR, FT-Raman, and UV-VIS techniques indicated a strong electronic interaction between V and W oxide species at the surface of the TiO_2 support. That interaction led to a higher reducibility of the ternary sample with respect to the corresponding binary ones. A synergism between V and W oxide surface species was suggested, which accounts for the high reactivity of the ternary samples in the SCR reaction. It was suggested that the higher reducibility of the samples, due to the electronic interactions between V and W and the TiO_2 support, was responsible for the higher reactivity of the ternary catalysts, particularly at low temperatures.

Topsøe (1995a and b) identified simultaneous information of the surface adsorbed species on vanadia/titania catalysts and the composition of reaction products

during the selective catalytic reduction of NO by in situ FT-IR and on line mass spectrometric studies. The experiments were carried out as temperature programmed surface reaction (TPSR) studies by exposing catalysts with preadsorbed ammonia to either pure NO, pure O_2 or a mixture of NO and O_2. That allowed detailed information to be obtained concerning the changes in the concentrations and the nature of the surface V=O and V-OH species. The SCR reaction was observed to take place during the TPSR studies in both NO and NO+O_2, but a greater rate was observed in the latter case. It was found that NH_3 reduces the V=O species and subsequent reaction with NO results in the formation of reduced V-OH species. The results showed that the NO reduction reaction involved the ammonia species adsorbed on V-OH Brönsted acid sites. Evidence for the importance of redox reactions was also found. Separate temperature programmed reduction (TPR) studies in H_2 showed that the surface vanadia layer breaks up while re-exposing TiOH groups. Subsequent temperature programmed oxidation (TPO) studied in O_2 showed that phenomenon to be completely reversible, thus providing direct evidence for spreading/redispersion of vanadia on titania. The TPR/TPO studies also indicated that the Brönsted acid sites essential for the deNO$_X$ reaction were associated with V^{5+}-OH surface sites.

Moreover, the reaction mechanism and catalytic cycle for the selective catalytic reduction of nitric oxide by ammonia over vanadia/titania catalysts had been elucidate by in situ on-line FTIR studies under steady-state conditions. Under all reaction conditions, a large concentration of ammonia was adsorbed on both Lewis and Brönsted acid sites whereas no significant amounts of adsorbed NO were adsorbed. The catalytic activity was found to be related to the ammonia adsorbed on Brönsted acid sites associated with V^{5+}-OH. Surface V=O groups were involved in activation of the adsorbed ammonia and were also found to play an important role in the catalytic cycle. The activation involved a transfer or a partial transfer of hydrogen and reduced V-OH groups are produced. The V^{5+}=O surface species were regenerated by oxidation. The results, therefore, showed that the catalytic cycle consists of both acid-base and redox reactions. The ammonia adsorption was observed to be a fast equilibrated step under all the conditions studied but the other significant catalytic steps might shift depending on the reaction conditions. At high

O_2 partial pressure, the rate was mainly determined by the concentration of Brönsted acid sites and the NO partial pressure, whereas at low O_2 partial pressures, surface reoxidation was slow and the rate became dependent on the concentration of $V^{5+}=O$ groups.

Ozkan and coworkers (1995) set up nitric oxide and oxygen exchange experiments and arrived at conclusions regarding the pathways of the SCR reactions. The role of ammonia oxidation had been quantified in the overall SCR reaction network at higher temperatures. They proposed a hydroxylamine species acting as a precursor for NH_3 oxidation to NO. They also proposed another species to be formed ammonia on vanadia-based catalysts (depicted as $V-ONH_3$) and produced by the reaction of $V=O + NH_3$. This species was supposed to be a precursor for N_2 and N_2O formation from ammonia or of N_2O from NH_3+NO.

Amiridis *et al.* (1995) showed that with H_2O and SO_2 in the feed stream, the SCR activity decreased with increasing vanadia loading. Samples of high activity all contained anatase TiO_2, but an active vanadia species only needed to be in close proximity and interacting with, and not necessarily deposited on the surface of crystalline titania. Co-gelling was thus an effective way to prepare an active sample in a single step, as demonstrated by the SCR data of the titania-vanadia aerogel. The addition of niobia, up to 10wt%, did not appreciably change the surface area, structure, or SCR activity of the titania aerogel supported vanadia.

Ramis and Busca (1996) studied the adsorption and transformation of ammonia over V_2O_5, V_2O_5/TiO_2, $V_2O_5-WO_3/TiO_2$, and CuO/TiO_2 systems by FT-IR spectroscopy. In all cases ammonia was first coordinated over Lewis acid sites and later undergoes hydrogen abstraction giving rise either to NH, amide species of to its dimeric form N_2H_4, hydrazine. Other species, tentatively identified as imide NH, nitroxyl HNO, nitrogen anions N^{2-} and azide anions N^{3-} were further observed over CuO/TiO_2. The comparison of the infrared spectra of the species arising from both NH_3 and N_2H_4 adsorbed over CuO/TiO, strongly suggested that N_2H_4 was an intermediate in NH, oxidation over this active selective catalytic reduction and

selective catalytic oxidation catalysts. That implied that ammonia was activated in the form of NH, species for both SCR and SCO, and it could later dimerize. Ammonia protonation to ammonium ion was detected over V_2O_5-based systems, but not over CuO/TiO_2, in spite of the high SCR and SCO activity of that catalyst. Consequently Brönsted acidity was not necessary for the SCR activity.

Dumesic and coworkers (1996) used a kinetic model based on a previously proposed reaction scheme to describe reaction kinetic measurements for the selective catalytic reduction of nitric oxide by ammonia over 6wt% vanadia/titania catalysts in the presence of oxygen (2 mol%) at nitric oxide and ammonia concentrations from 100 to 500 ppm and at temperatures of 250 °C and 300 °C. That reaction scheme involved adsorption of ammonia on Brönsted acid sites (V^{5+}-OH), followed by activation of ammonia via reaction with redox sites (V=O). That activated form of ammonia reacted with gaseous or weakly adsorbed NO, producing N_2 and H_2O, and leading to partial reduction of the catalyst. The V^{4+}-OH species formed by the selective catalytic reduction reaction combine to form water, and the catalytic cycle was completed by reaction of the reduced sites with O_2. Water adsorbed competitively with ammonia on acid site. That reaction scheme had been used to describe the kinetics of the SCR reaction under laboratory as well as under industrially relevant reaction conditions.

Ciambelli *et al.* (1996) investigated the effect of sulphate on the catalytic properties of V_2O_5/TiO_2 and WO_3/TiO_2 in the selective reduction of NO with NH_3. For both catalytic systems, the presence of sulphate resulted in the enhancement of catalytic activity without reduction of selectivity to nitrogen. The rate of NO reduction depended on the sulphate content, which was affected by the original composition of titania, the method of catalyst preparation and the metal oxide loading.

Amiridis *et al.* (1996) studied the selective catalytic reduction of NO by NH_3 over V_2O_5/TiO_2 catalysts of variable vanadia loading in the presence and the absence of H_2O and SO_2. Under dry and SO_2 free conditions, the turnover frequency of the SCR reaction was found to go through a maximum with vanadia surface coverage at

approximate half a monolayer. They also observed that decreased in the SCR turnover frequency at vanadia surface coverages exceeding half a monolayer could be attributed to the loss of strong acid sites which were associated with the TiO_2 support. Addition of H_2O to the reacting gas mixture, decreased in the SCR turnover frequency of approximately 40-50%, which was independent adsorption of H_2O on the active vanadia sites, The presence of SO_2 in the gas phase during the SCR reaction results in a significant increase of the turnover frequency at low vanadia surface coverages, while it had no effect of SO_2 could be attributed to the formation of surface sulfate species, which were only present on the titania surface below half a monolayer coverage due to repulsive interactions between the surface vanadia and sulfate species.

Hu and Apple (1996) investigated the adsorption of nitric oxide by ammonia over a series of V_2O_5/TiO_2 catalysts used for selective catalytic reduction by solid-state N^{15} NMR. The chemistry and the surface acidity were found to vary dramatically as the weight loading of vanadia was increased from 0 to 10%. NO reacts over evacuated TiO_2 and V_2O_5/TiO_2 at room temperature to form nitrous oxide (N_2O). Over the V_2O_5/TiO_2 catalysts N_2 was also produced upon room temperature adsorption. The chemical shift of the terminal nitrogen of N_2O adsorbed on the catalyst was an indicator of the Lewis acid character of the surface. The Lewis acidity of the surface was found to decrease with the loading of V_2O_5 on the titania support. Ammonia adsorbed in two forms on evacuated TiO_2 and V_2O_5/TiO_2. Those two forms differed in their surface mobility. The reaction of NO with NH_3 over the catalysts proceeded to a measurable degree at room temperature. N_2 was the predominant product, however, N_2O was also produced by the partial reduction of NO. Following preadsorbtion of ammonia, the chemical shift of the terminal nitrogen of N_2O was similar to that of samples with a high V_2O_5 loading regardless of the actual vanadia loading. That indicated that ammonia was adsorbed predominantly on the Lewis acid sites of the catalyst, blocking the access of N_2O to those sites.

The effect of SO_2 on the activity for the selective catalytic reduction of NO with NH_3 over V_2O_5/TiO_2 catalysts, both unpromoted and promoted by Nb_2O_5, had

been studied by Kijlstra and coworkers (1996) at temperature below 200 °C. They showed that enhanced Brönsted acidity due to the formation of surface sulphates promoted the SCR activity whereas deposition of ammonium(bi)sulphates might cause severe deactivation. The combination of activity tests, TPD and FT-IR showed that both effects occurred simultaneously at that low temperature. The support morphology, the presence of Nb_2O_5 and especially the V_2O_5 loading determined the net effect of SO_2 in terms of activity.

Lietti and coworkers (1996a-d) studied the physico-chemical characteristics and the reactivity of V_2O_5-WO_3/TiO_2 catalysts. They indicated that tetravalent vanadium ions both in magnetically isolated form and in clustered, magnetically interacting form were present over the TiO_2 surface. The presence of tungsten oxide stabilized the surface V^{5+} and modifies the redox properties of V_2O_5/TiO_2 samples. Ammonia adsorbd on the catalysts surface in the form of molecularly coordinated species and of ammonium ions. Upon heating, activation of ammonia via an amide species apparent. V_2O_5-WO_3/TiO_2 catalysts exhibited higher activity than the binary V_2O_5/TiO_2 and WO_3/TiO_2 reference sample. That was related to both higher redox properties and higher surface acidity of the ternary catalysts. Results suggested that the catalyst redox properties control the reactivity of the samples at low temperatures whereas the surface acidity played an important role in the adsorption and activation of ammonia at high temperatures. The catalyst redox properties appeared as a key-factor in controlling the reactivity of V_2O_5-WO_3/TiO_2 catalysts at low temperatures.

Andrini *et al.* (1996) demonstrated that increasing the vanadia loading, or surface vanadia coverage, increased the acidity and reactivity of the V_2O_5/Al_2O_3 catalysts. Introducing additived (Mo, W, Ni, and Co) that did not influence the Brönsted acidity, Mo oxide and W oxide, also increased the reactivity. However, the addition of Ni oxide and Co oxide increased the ratio of polymerized to isolated surface vanadium oxide species on alumina, which revealed that the SCR reaction was not sensitive to the surface vanadia structure on alumina. A model that explained those observations consists of a dual site: a surface redox site and an adjacent surface Brönsted acid site. Consequently, increasing the surface vanadium oxide coverage

and introducing additives that increased the surface concentration of Brönsted acid sites was beneficial for the SCR of NO with NH_3.

Wachs and coworkers (1996) investigated the influence of surface vanadia coverage, promoters (surface tungsten oxide, niobium oxide, and sulfate species), and the specific oxide support(TiO_2, Al_2O_3 and SiO_2). The findings suggested that a dual-site (a surface vanadia redox site and an adjacent nonreducible metal oxide sites) mechanism was required for the efficient selective catalytic reduction of NO with NH_3 over supported vanadia catalysts. The SCR reaction was sensitive to the immediate environment of the surface vanadia species. The SCR selectivity toward N_2 formation also varied with the immediate environment of the surface vanadia species. The selectivity depended on the specific oxide support (TiO_2 > Al_2O_3 > SiO_2), temperature (decreases with the concentration of pairs of redox sites). The SCR reaction was not related to the properties of the terminal V=O bond since in situ Raman studies during SCR, employing $V=O^{18}$, demonstrated that this bond was relatively stable under reaction conditions (possessing a lifetime that is similar to 10 times the characteristic reaction time), Thus, the bridging V-O-support bond appeared to be involved in the rate-determining step.

Tac et al. (1997) studied the thermal deactivation and structural specificity of V_2O_5/TiO_2 catalysts in the selective catalytic reduction of nitric oxides. They indicated that the 72 hours heat treatment at the temperature of 420 and 480 °C had no significant effect on the bulk density, density, pore volume and phase composition of catalyst. The surface area of samples decreased dramatically. The relation of reaction rate preexponent constant to the specific surface area could be used as a measure of deactivation.

Paganini and coworkers (1997) , using the electron paramagnetic resonance spectroscopy, investigated the activity and selectivity in the selective catalytic reduction of nitric oxide. All the systems exhibited the spectra due to the presence of both isolated and magnetically interacting V^{4+} ions whose amount had been monitored as a function of the temperature of progressively reducing vacuum

treatments. By comparison with binary systems (V_2O_5/TiO_2 and WO_3/TiO_2) evidence had been provided for the interaction with the TiO_2 matrix. The present investigation revealed the existence of a mutual (structural and electronic) systems. Those properties were remarkably different from that of V_2O_5/TiO_2 systems and could contribute to an understanding of the catalytic behavior of the V_2O_5-WO_3/TiO_2 systems in the SCR reaction.

Gilardoni and coworkers (1997) modeled the mechanism of selective catalytic reduction of NO by NH_3 on a supported vanadium oxide monolayer. In the first step, the adsorption of NH_3 on a bimetallic cluster representative of vanadium oxide, containing a terminal V=O adjacent to a V-OH group, was investigated. The calculations indicated that NH_3 might be strongly adsorbed on V-OH (Brönsted acid site) as NH_4^+(ads); subsequently, NO reacted with that activated NH_3 to yield the reaction products N_2 and H_2O. The results gave support to a dual-site Eley-Riedal-type mechanism involving a Brönsted site.

Lietti *et al.* (1998) studied the unsteady state kinetics of NH_3 adsorption-desorption and of selective catalytic reduction of NO with NH_3 on V_2O_5/TiO_2 and V_2O_5-WO_3/TiO_2 catalysts by transient response techniques. Over both catalysts the dynamic experiments could be successfully described by a kinetic model assuming; (1) negligible NO adsorption on the catalyst surface; (2) nonactivated NH_3 adsorption; (3) a Temkin-type NH_3 coverage dependence of the desorption energy; (4) a nonlinear dependence of the SCR reaction rate on the NH_3 surface coverage. Thus, the results were supportive of an Eley-Riedel mechanism for the SCR reaction and of a significant heterogeneity for adsorption-desorption process and surface reaction of the catalyst surface. The binary and ternary catalysts exhibited similar acid properties, but different activity in the SCR reaction, possibly related to the superior redox properties of the WO_3 containing sample. Over both samples, the estimates of the activity energies for NH_3 desorption at zero coverage and for the surface reaction of NO with NH_3 were similar and in the 96.14-108.68 and 58.52-66.88 kJ/mole ranges, respectively.

An in situ diffuse reflectance FT-IR spectroscopy (DRIFTS) study of the selective catalytic reduction of with NH_3 in the presence of O^{2-} had been carried out by Centeno *et al.* (1998) over vanadia/alumina and vanadia/lanthanide-doped alumina catalysts. The SCR reaction data might be interpreted on the basis of an Eley-Riedel type mechanism between gaseous NO and adsorbed ammonia species (NH^{4+} and/or coordinated NH_3). Although both adsorbed ammonia species seem to be reactive, NH^{4+} groups were more effective in the SCR reaction. Thus, at the temperature of the highest NO conversion (T-max), ammonia was adsorbed preferentially as NH^{4+} over the undoped catalyst, meanwhile over lanthanide-doped ones, the adsorption of coordinated NH_3 became predominant, thus explaining the lower SCR activity of such type of catalysts. At lower temperatures, NO was adsorbed as nitrates and the NH_3 adsorption as coordinated NH_3 species was enhanced. Those two factors drove the activity decrease.

Dunn (1998) studied the supported vanadia SCR catalysts on various metal-oxide supports: ceria, zirconia, titania, alumina and silica. It was concluded that at low vanadia loadings, vanadia preferentially exists on oxide support surfaces as isolated tetrahedrally coordinated $(M-O)_3V^{5+}O$ species. At higher vanadia loading, the isolated $(M-O)_3V^{5+}O$ species polymerize on the oxide support surface breaking two V-O-M bonds and forming two V-O-V bridging bonds. The turnover frequency for sulfur dioxide oxidation was very low, 10^{-4}-10^{-6} s^{-1} at 400 °C, and was independent of vanadia coverage suggesting that only one vanadia site was required for the oxidation reaction. As the support was varied, sulfur dioxide oxidation activity of the supported vanadia catalysts varied by one order of magnitude (Ce>Zr, Ti>Al>Si). The basicity of the bridging V-O-M oxygen appeared to be responsible for influencing the adsorption and subsequent oxidation was zero-order in oxygen, first-order in sulfur dioxide molecule. Over the range of conditions studied, the rate of sulfur dioxide oxidation was zero-order in oxygen, first-order in sulfur dioxide and inhibited by sulfur trioxide. The turnover frequency for sulfur dioxide oxidation over WO_3/TiO_2 was an order of magnitude lower than that found for V_2O_5/TiO_2, and no redox synergism between the surface vanadia and tungsten oxide species was evident for a ternary V_2O_5-WO_3/TiO_2 catalyst. That suggested that WO_3 promoted catalysts

might be suitable for low temperature SCR where minimal sulfur dioxide oxidation activity was required.

Kamata and coworkers (1998) examined influence of phosphorus in the commercial V_2O_5-WO_3/TiO_2 SCR catalyst. Phosphorus added to the catalyst was found to disperse well over the catalyst without a significant agglomeration up to 5wt%P_2O_5 addition. The number of the hydroxyl groups bonded to the vanadium and titanium species decreased readily with increasing amount of phosphorus. Correspondingly the hydroxyl groups bonded to the phosphorus species were formed. NH_3 adsorbed on both hydroxyl groups bonded to vanadium and phosphorus as ammonium ions, implying that the P-OH groups formed are also responsible for the Brönsted acidity. The NO reduction activity was found to be decreased with increasing amount of phosphorus; however, the influence of phosphorus was relatively small irrespective of the large amount of phosphorus addition. The deactivation might be caused by the change in the nature of the surface hydroxyl groups, which might also contribute to the deactivation.

Lietti (1998) investigated the chemico-physical characteristics and the catalytic activity of commercial and home-made V_2O_5-WO_3/TiO_2 catalysts. The samples were constituted by TiO_2 anatase that supported the V and W components (and S in the case of commercial catalysts). The V+W estimated surface coverage was below that corresponding to the theoretical monolayer, but when surface sulfates were also taken into account the monolayer capacity of the samples was expected. V,W and sulfates were present on the dry catalyst surface in the form of isolated vanadyl, wolframyl and sulfate species, all in a mono-oxo type form. The adsorption-desorption study showed that NO did not absorb on the catalyst surface, whereas NH_3 adsorbed on both Lewis and Brönsted acid sites. Lewis bonded NH_3 species were thermally more stable than ammonium ions, and upon heating, a weak band was observed at 1540 cm^{-1}, that had been assigned to an amide species NH_2. When NH_3 covered surface was heated in the presence of NO, ammonia was activated on Lewis acid sites and then reacted with gas-phase NO to give N^{2-}. Mechanistic features of the selective catalytic reduction (SCR) reaction had also been collected by means of

transient methods, including the temperature programmed desorption/reaction techniques and the transient response analysis (TRA). Those experiments proved that: (i) the reaction occurred between adsorbed ammonia and gas-phase or weakly adsorbed NO; (ii) NH_3 could not only adsorb over the active V-sites but also on the surface W- and Ti-sites and on surface sulfates as well, hence acting as an ammonia "reservoir", (iii) the mechanism is of the redox type, *i.e.* oxygen oxidizes the surface sites reduced by the other reactants.

Orsenigo *et al.* (1998) performed the transient experiment over synthesized and commercial V_2O_5-WO_3/TiO_2 catalysts during catalyst conditioning and during step changes of the operating variables (SO_2 inlet concentration and temperature). It was shown that conditioning of the catalyst was required to attain significant and reproducible steady-state data in both the reduction of NO_x and the oxidation of SO_2. The response time of conditioning for NO_x reduction was of a few hours and that for SO_2 oxidation was of several hours. Fourier transform infrared spectroscopy temperature programmed decomposition, and thermogravimetric measurements showed that catalyst conditioning times observed in the reduction of NO_x and in the oxidation of SO_2 suggested that the build up of sulfates occurred first at the vanadyl sites and later on at the exposed titania surface. Formation of sulfates at or near the vanadyl sites increased the reactivity in the de-NO_x reaction, possibly due to the increase in the Brönsted and Lewis acidity of the catalyst, whereas the titania surface acts as SO_3 acceptor and affects the outlet SO_3 concentration during catalyst condition for the SO_2 oxidation reaction. The response time to step changes in SO_2 concentration and temperature was of a few hours in the case of SO_2 oxidation and much shorter in the case of NO_x reduction. The different time responses associated with conditioning and with step changes in the settings of the operating variables had been rationalized in terms of the different extent of perturbation of the sulfate coverage experienced by the catalyst.

2.2 Some comments on the previous works

The reviewed literatures show that among of several catalyst systems studied, vanadium(V)oxide supported on titanium(IV)oxide catalyst is the most widely employed is SCR process. Though the V_2O_5/TiO_2 system posses high SCR activity, its performance can be further enhanced by adding metal oxides *e.g.* oxides of W, Mo, Nb, Ge, and Y [*e.g.* Chen and Yang 1992, Weng and Lee 1993, and Oderbrand *et al.* 1994]. Several proposals [*e.g.* Inomata *et al.* 1980, Janssen *et al.* 1987a-b, Ozkan *et al.* 1993, Ramis *et al.* 1990, Topsøe *et al.* 1995a-b, and Busca *et al.* 1998] in the literature concerning the mechanisms of the SCR reaction over vanadia-based catalysts were proposed that the SCR reaction involved a strongly adsorbed NH_3 species and a gaseous or weakly adsorbed NO species, but differ from the nature of the adsorbed reactive ammonia species and of the associated reaction intermediate. Protonated ammonia and molecularly coordinated ammonia have been envisaged as the reactive ammonia surface species. In the former case gaseous or weakly bound NO attacks the nitrogen of protonated ammonia via the N atom of NO, giving rise to an intermediate reactive species [Ramis *et al.* 1990]. However its nature has not been fully clarified so far. In the latter case coordinated ammonia is activated through hydrogen abstraction to an amide species, possibly a radical amide species, that abstraction to an amide species, possibly a radical amide species, that may couple with the radical NO species to form NH_2NO that eventually decomposes to N_2 and H_2O. [Inomata *et al.* 1980, Janssen *et al.* 1986, and Topsøe 1995 a-b] The above two mechanistic proposals correlate the catalyst activity to different acid sites (Brönsted versus Lewis acid sites). In additional, the surface acidity of the catalysts under reaction conditions is strongly influenced by the presence of water and is further modified upon adsorption of SO_3, due to the occurrence of the SO_2 oxidation, including poisoning by alkali metals that are present is fly ashes [Chen and Yang 1990, Tokarz *et al.* 1991, and Lietti *et al.* 1993b].

Accordingly, this thesis is interested in the effect of acidity property of V_2O_5/TiO_2 with tungsten and potassium loading for selective catalytic reduction.