

CHAPTER II

LITERATURE REVIEWS

The selective catalytic reduction (SCR) of NO_x with ammonia is currently of great interest because of the desire to minimize pollution from stationary emissions related to acid rain formation. Though catalysts based on $\text{V}_2\text{O}_5/\text{TiO}_2$ has been extensively employed in industrial practice, the review in this chapter will concentrate on those used in elimination NO_x from flue gas.

2.1 Reviews paper

In this section, the relevant selective catalytic reduction (SCR) of NO_x with ammonia by $\text{V}_2\text{O}_5/\text{TiO}_2$ paper are concluded for leading to raise the problem issue. The significant previous paper are as follows :

Murakami et. al. [12] studied effect of supported vanadium oxides prepared by both the conventional impregnation and vapour-phase-supporting methods ; TiO_2 (anatase), TiO_2 (rutile), TiO_2 (mixture of anatase with rutile), Al_2O_3 , ZrO_3 , SiO_2 and MgO were used as supports. It was found that the structure of the vapour-phase-supporting catalyst does not change significantly from that of the catalyst prepared by the conventional impregnation method. Also, the structure of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst does not change significantly with the modification of TiO_2 , i.e. anatase, rutile and

mixture of anatase with rutile. This mean that the difference in the modification of TiO_2 is too small to affect the structure of V_2O_5 on the support. On the other hand, the structure of supported vanadium oxide catalyst is greatly changed with the kind of support, i.e. TiO_2 , Al_2O_3 , ZrO_3 , SiO_2 and MgO . In conclusion, that the structure of supported vanadium oxide is mainly determined by the kind of support, while neither the method of preparation nor the modification of support affects the structure significantly.

Kotter et.al. [13] investigated structure and selectivity changes in vanadia-titania catalysts used to promote the reduction of nitric oxide with ammonia. Heat treatment of vanadia-titania (anatase) catalysts of temperatures lower than those required for the anatase-rutile transformation has been found to cause changes in the structure of the catalysts and the selectivity for the reduction between ammonia and nitric oxide. As the treatment temperature increased from 350 to 440°C, and as the time of heat treatment increased, the surface area decreased, the amount of vanadia (V) species weakly interacting with titania increased and needle-like crystals were formed. At the same time, the reduction of nitric oxide to nitrogen decreased while formation of nitrous oxide is promoted. Washing the catalyst with ammonia solution removed the crystal deposited and cloud avoid the production of nitrous oxide.

Cai et. al. [14] investigated selective catalytic reduction (SCR) of nitric oxide with ammonia over both phases of titania (Anatase and Rutile). It was found that vanadia catalysts supported over (anatase and rutile) phases of titania showed high

activity and selectivity for selective catalytic reduction of nitric oxide at relatively low temperatures although catalysts supported over the rutile phase appeared to be more active on a unit surface area basis. The activity of the catalyst went through a maximum with increasing loading levels, over both supports. A coordinated polymeric surface species of vanadia, which was detected through laser Raman spectroscopy and observed on both anatase and rutile phases, appeared to be more active than bulk V_2O_5 for the desired reaction. The X-ray diffraction pattern obtained from catalysts supported over both phases of TiO_2 , showed the presence of crystalline V_2O_5 at loading levels of 6.6 % or higher. For catalysts supported over both phases of TiO_2 , the presence of crystalline V_2O_5 did not seem to affect the catalytic activity significantly.

Tufano et. al. [15] studied selective nitric oxide reduction over a high-surface area V_2O_5 - TiO_2 catalyst in the range 200-350°C, at different initial NH_3/NO ratios and contact times, in the presence of excess oxygen. The experimental conversion-time data were compared with different kinetic models developed on the basis of information from the literature. For the two best model the reliability of the results of the present kinetic analysis confirmed that nitric oxide reduction over V_2O_5/TiO_2 catalysts, by kinetic model (1). In this case, nitrosamidic intermediate model leads to the kinetic model :

$$R_N = (k_c * K_N * P_N * K_A * P_A) / (1 + K_A * P_A * (1 + K_N * P_N)) \quad (1)$$

and kinetic model (2) Correspondingly, the effect of water and nitrosamidic intermediate leads :

$$R_N = (k_c * K_N * P_N * K_A * P_A) / (1 + K_A * P_A * (1 + K_N * P_N) + K_W * P_W) \quad (2)$$

Lintz et. al. [16] investigated intrinsic kinetics of nitric oxide reduction by ammonia on a vanadia-titania catalyst. In conclusion, the reduction of nitric oxide by ammonia in the presence of oxygen can be described by the use of three linearly independent stoichiometric equations, including nitrous oxide formation and ammonia combustion. The addition of water in flue gas slightly reduced the catalyst activity but caused decisive increase of the selectivity. On the other hand the possible side reactions, the oxidation of ammonia and the formation of nitrous oxide were largely suppressed by the presence of water. The investigation of transport phenomena has showed that a strong influence of inner mass transfer resistance was expected in catalysts of technically relevant dimensions. The intrinsic kinetics can be quantified by use of a Langmuir-Hinshelwood type rate equation.

Ozkan et. al. [17] studied selective catalytic reduction (SCR) of nitric oxide with ammonia over vanadium pentoxide catalysts with preferential exposure of different crystal planes. Results from the blank reactor experimental performed at the beginning of the kinetic studies showed no measurable contribution from homogeneous reaction or reactor wall activity. The fact that the catalysts showed essentially no porosity and that they were used in the reactor without pelletizing

allowed them to rule out any diffusion limitations. Therefore, the results indicated that vanadium pentoxide catalysts which exhibited preferred exposure of different crystal planes showed marked differences in their catalytic performance in SCR reactions. While characterization results showed that major difference between these catalysts was the relative abundance of V=O sites, the kinetic studies indicate that the ammonia adsorption took place on at least two different sites located on the basal and side planes. The differences found in the product distribution were explained by considering a complex network of reactions which involves both V=O sites and V-O-V sites and which included both selective reduction of nitric oxide and direct oxidation of ammonia. Another interesting feature of the results is increasing the total flow-rate did not seem to affect the product distribution and the trends for relative rates of conversion of nitric oxide and ammonia significantly, indicating no significant mass transfer limitations.

Weng et. al. [18] examined catalytic performance and active sites determination of niobium oxide promoted vanadia-titania catalysts for selective catalytic reduction of nitric oxide with ammonia. It was found that the addition of Nb₂O₅ to V₂O₅/TiO₂ catalysts increased both Lewis acid and Brønsted acid sites with the content of Nb₂O₅ on the catalyst due to the increase in BET surface area, in which the Brønsted acid sites were more significant for the SCR reaction. As a result to enhancement of the catalytic activity in the SCR reaction and ammonia oxidation in the lower and higher temperature ranges, respectively. Due to the Nb₂O₅ promoted vanadium/titania catalysts.

Dumesic et al. [19] evaluated different mechanisms in a kinetic analysis of the DeNO_x reaction. It was shown that a simple two-step Eley-Rideal mechanism involving reaction between adsorbed NH₃ and gaseous (or weakly adsorbed) NO is not consistent with all data. Therefore, they proposed a three-step mechanism consisting of equilibrated ammonia adsorption, followed by an activation step of the adsorbed ammonia and a subsequent reaction between the activated ammonia species and NO. It was shown that it was not possible to distinguish kinetically whether this last step was a true Eley-Rideal step involving reaction with gaseous NO or a reaction with weakly adsorbed NO. The three-step mechanism was able to quantitatively describe the NO conversion data under industrial-type conditions for the vanadia/titania catalysts. Furthermore, it gave at the same time a very good description of the ammonia slip behavior which was found to be much more difficult to describe than the conversion of NO_x. Although this mechanism was also shown to be consistent with several independent observations, it can still be regarded as semi-empirical in nature due to the fact that detailed information on the surface chemistry was not available at the time.

Vikulov et al. [20] reported that selective catalytic reduction (SCR) of nitric oxide with ammonia over Nb₂O₅-promoted V₂O₅/TiO₂ catalyst. In contrast to previous claims of Tanabe et al. [21], the addition of niobia to catalysts containing vanadia supported on titania resulted in much enhanced activity for low-temperature SCR of nitric oxide with ammonia only at low vanadia loadings. Niobia promoted catalysts could also be demonstrated to show higher selectivities to N₂, especially at

high temperature and low vanadia loading. This enhancement of the activity would not be explained only on the basis of the observation that niobia stabilized the surface area of catalyst. Calculations of the activation energy suggested that a different mechanism of the reaction may be at work at low vanadia loadings.

Turco et. al. [22] investigated the influence of water on the kinetics of nitric oxide reduction with ammonia over V_2O_5/TiO_2 catalyst at different water partial pressure (0-300 Pa), with the aim of developing a kinetic model able to describe the influence of water on the reaction rate of nitric oxide reduction with ammonia. The results obtained in this work showed that water played an important role in the kinetics of nitric oxide reduction by ammonia over V_2O_5/TiO_2 catalysts, producing an inhibiting effect on the reaction rate. This effect was properly described by a kinetic model based on the hypothesis of the formation of a nitrosamic intermediate and of irreversible adsorption of water on energetically not equivalent sites. It has been found that a kinetic model based on the irreversible adsorption of water following a Temkin isotherm allows the kinetics of nitric oxide reduction to be described well the inhibition due to water on nitric oxide conversion either when the water was only formed by the reaction, or when it was fed in large excess to the reactor. These results were interpreted according to a poisoning effect of the ammonia adsorbing sites by water. Finally, they had concluded that the nitric oxide reduction over V_2O_5/TiO_2 catalysts occurred through a complex mechanism involving NO, NH_3 and H_2O as adsorbed species.

Matralis et. al. [11] studied the influence of the MoO_3 content on their catalytic performance for the selective catalytic reduction (SCR) of nitric oxide by ammonia in the presence of oxygen, as well as on their textural and structure properties. They reported that the coverage of the TiO_2 support by surface polymeric molybdenum species (where molybdenum was octahedrally coordinated) increased with the molybdenum loading. The formation of a layer of these interacting species on top of the titania surface completed in the range 15-20 wt. % MoO_3 . The formation of crystallites of bulk MoO_3 started before the completion of this surface layer (at around 10 wt.% MoO_3) and increased progressively as the molybdenum loading increases from 10 to 20 wt.% MoO_3 . The SCR activity of the $\text{MoO}_3/\text{TiO}_2$ catalysts increased as the MoO_3 content increased to 15 wt.% and then, for a further increase of the molybdenum loading, it slightly decreased. No specific influence of the molybdenum content on the resistance of catalysts towards SO_2 . Their results indicated that the octahedrally coordinated polymeric molybdenum surface species are mainly responsible for the exhibited SCR activity of the $\text{MoO}_3/\text{TiO}_2$ catalysts.

Marrshneva et. al. [23] investigated the influence of support on activity of monolayer vanadia-titania catalysts for selective catalytic reduction (SCR) of nitric oxide by ammonia. The vanadia-titania catalyst were prepared via VOCl_3 grafting on the TiO_2 surface, $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalysts were prepared by inserting ammonia salt in TiO_2 . It has found that the specific activity, activation energy, and turnover frequency did not depend substantially on the crystal structure of titania. The SCR reduction on titania-supported vanadia hardly depended on the concentration of

vanadium atoms. NO reduction by ammonia with gaseous oxygen (SCR) and without oxygen showed the same activation energy for supported vanadia, and nearly coincides with vanadia reoxidation activation energy. Reoxidation of reduced vanadia species (V-OH) seemed to be the rate-limiting step of the SCR process. Finally, reduction of nitric oxide by ammonia with and without oxygen may have a common reduction mechanism with peculiar step involving reoxidation by gaseous oxygen and nitric oxide and different surface V=O concentrations.

Topsøe et al. [24] combined in situ FT-IR and on-line mass spectrometric studies provide simultaneous information of the surface adsorbed species on the vanadia/titania catalysts and the composition of reaction products during the selective catalytic reduction (SCR) of NO. The experiments were carried out as temperature programmed surface reaction (TPSR) studies by exposing catalysts with preadsorbed ammonia to either pure NO, pure O₂, or a mixture of NO and O₂. This technique 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 TPSR studies in O₂ showed mainly ammonia desorption and some ammonia oxidation at the high temperatures. The SCR reaction was observed to take place during the TPSR studies in both NO and NO+O₂, but a greater rate was observed in the latter case. It was found that NH₃ 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 involves the ammonia species adsorbed on V-OH Brønsted 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 Ti-OH groups. Subsequent temperature programmed oxidation (TPO) studies in O_2 showed this phenomenon to be completely reversible, thus providing direct evidence for the spreading/redispersion of vanadia on titania. The TPO/TPR studies also indicated that the Brønsted acid sites essential for the $DeNO_x$ reaction are associated with V^{5+} -OH surface sites.

Topsøe et al. [25] elucidated the reaction mechanism and catalytic cycle for the selective catalytic reduction of nitric oxide by ammonia over vanadia /titania catalysts with in situ on line FT-IR studies under steady state conditions. Under all reaction conditions, a large concentration of ammonia was adsorbed on both Lewis and Brønsted acid sites, whereas no significant amounts of adsorbed NO were adsorbed. The catalytic activity was found to be related to the ammonia adsorbed on the Brønsted acid site associated with V^{5+} -OH. Surface V=O groups were involved in activation of the adsorbed ammonia and also found to play an important role in the catalytic cycle. The activation involved a transfer or a partial transfer of a hydrogen and reduced V-OH groups were produced. The V=O surface species were regenerated by oxidation. The results, therefore, showed that the catalytic cycle consisted 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 catalytically significant steps may shift depending on the reaction conditions. At high O_2 partial pressures, the rate was mainly determined by the concentration of Brønsted acid sites and NO partial

pressure, whereas a low O_2 partial pressures, surface reoxidation was slow and the rate became dependent on the concentration of $V=O$ groups.

Jehng et al. [26] investigated the effect of water vapor on the molecular structures of V_2O_5 -supported catalysts (SiO_2 , Al_2O_3 , TiO_2 , and CeO_2) by in situ Raman spectroscopy as a function of temperature (from 500 to 120°C). Under dry conditions, only isolated surface VO_4 species were present on the dehydrated SiO_2 surface, and multiple surface vanadium oxide species (isolated VO_4 species and polymeric vanadate species) were present on the dehydrated Al_2O_3 , TiO_2 , and CeO_2 surface. The Raman features of the surface vanadium oxide species on the SiO_2 support were not affected by the introduction of water vapor. This indicated that the molecular structure of the surface vanadium oxide species on SiO_2 was not affected by the presence of water vapor due to the hydrophobic nature of the SiO_2 (Cab-O-Sil) support. However, the presence of water had a pronounced effect on the molecular structures of the surface vanadium oxide species on the Al_2O_3 , TiO_2 , and CeO_2 supports. The Raman band of the terminal $V=O$ on this oxide supports shifted to lower wavenumbers by 5-30 cm^{-1} and became broad compared to that under dry conditions. Above 230°C, the Raman shift of the surface vanadium oxide species in the presence of water suggests that the dehydrated surface VO_x species formed a hydrogen bond with some adsorbed moisture. The hydrogen-bonded surface VO_x species were extensively solvated by water molecules and formed a hydrated surface vanadate structure upon further decreasing the temperature below 230°C (e.g., decavanadate). The Raman band in the 800-900 cm^{-1} region, which is characteristic

of the polymerized V-O-V functionality, appeared to be little influenced by the presence of this Raman band. Oxygen-18 isotopic labeling studies revealed that both the terminal V=O and polymeric V-O-V bonds readily undergo oxygen exchange with moisture. The current observations accounted for the inhibiting effect of moisture upon oxidation reactions over supported vanadia catalysts.

Kijlstra et. al. [27] reported the effect of SO₂ on the activity for the selective catalytic reduction (SCR) of nitric oxide with ammonia over V₂O₅/TiO₂ catalysts, both unpromoted and promoted by Nb₂O₅ at temperatures bellows 200°C. In literature, results were showed that at temperatures below 200°C, the surface of V₂O₅/TiO₂ catalysts could be sulphated by SO₂, leading to enhanced Brønsted acidity and to a higher SCR activity. On the other hand, SO₂ oxidation followed by (NH₄)₂SO₄ deposition led to deactivation of the catalysts. At low V₂O₅ loadings the former effect dominated, whereas at higher loadings deactivation by ammonia sulphates overruled promotion. Doping with Nb₂O₅ did not suppress SO₂ oxidation. At low V₂O₅ loadings, Nb₂O₅ covered the exposed TiO₂ surface, partly blocking the formation of (TiO)₃S=O. On a crystalline support Nb₂O₅ may promote both SCR activity and SO₂ oxidation, whereas it did not exert any effect on an amorphous support. The use of a crystalline support enhanced both the promoting and the deactivating effect. The use of a low loaded V₂O₅ catalyst on a crystalline support without Nb₂O₅, exhibiting a modest SCR activity after preparation, was advantageous if a stable SCR activity in SO₂-containing the gases below 227 °C was desired.

Ramis et al. [28] investigated 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 FTIR spectroscopy. In all cases ammonia was first coordinated over Lewis acid sites and later underwent hydrogen abstraction giving rise either to NH_2 amide species or 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_2 strongly suggested that N_2H_4 was an intermediate in ammonia oxidation over this active selective catalytic reduction (SCR) and selective catalytic oxidation (SCO) catalysts. This implies that ammonia was activated in the form of NH_2 species for both SCR and SCO, and it could later dimerize. Ammonia protonation to ammonium ions was detected over V_2O_5 -based systems, but not over CuO/TiO_2 , in spite of the high SCR and SCO activity of this catalyst. Consequently, Brønsted acidity was not necessary requirement for SCR and SCO activity, although it can favor it, when present, by favoring the adsorption of ammonia on the coordinative sites.

Lietti et al. [29] studied the physico-chemical characteristics and the reactivity of submonolayer $V_2O_5-WO_3/TiO_2$ DeNO_x catalysts by EPR, FT-IR, and reactivity tests under transient conditions. EPR indicated that tetravalent vanadium ions both in magnetically isolated form and in clustered, magnetically interacting form grafted on the matrix of TiO_2 surface. The presence of tungsten oxide stabilized the surface V^{5+} and apparently modified the redox properties of V_2O_5/TiO_2 samples in that the ternary

samples showed an higher reducibility than the corresponding vanadia/titania samples. Ammonia adsorbed over the ternary catalysts in the form of molecularly coordinated species and of ammonium ions, this latter species showing lower thermal stability. Upon heating, activation of ammonia via an amide species was also suggested. V_2O_5 - WO_3/TiO_2 catalysts exhibited higher activity in the SCR reaction than the corresponding binary vanadia/titania and tungsten oxide/titania reference samples; this has been related to both the higher redox properties and the higher surface acidity of the ternary catalysts. Results suggested that the catalyst redox properties control the reactivity of the ternary samples at low temperatures whereas the surface acidity plays an important role in the adsorption and activation of ammonia at high temperatures.

2.2 Some comment on a previous paper

From the reviewed literatures we can see that most works concentrated on catalyst with low vanadium oxide loading. Although this catalyst shows very good SCR activity in the temperature range 50-300°C, it suffers a serve draw back from its too high activity for NH_3 oxidation in the temperature over 300°C. The over oxidation of NH_3 is believed to be caused by the very active V=O species of monolayer V_2O_5 . However, the V=O species of crystalline V_2O_5 is not no active for the SCR and also NH_3 oxidation. Therefore, the V=O species exists on vanadium oxide surface between monolayer and crystalline oxide may exhibit a compromise activity.