

Review

# Chemical and mechanistic aspects of the selective catalytic reduction of NO<sub>x</sub> by ammonia over oxide catalysts: A review

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## Abstract

The open literature concerning chemical and mechanistic aspects of the selective catalytic reduction of NO by ammonia (SCR process) on metal oxide catalysts is reviewed. Catalytic systems based on supported V<sub>2</sub>O<sub>5</sub> (including the industrial TiO<sub>2</sub>-supported V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> and/or V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> catalysts) and catalysts containing Fe<sub>2</sub>O<sub>3</sub>, CuO, MnO<sub>x</sub> and CrO<sub>x</sub> are considered. The results of spectroscopic studies of the adsorbed surface species, adsorption–desorption measurements, flow reactor and kinetic experiments are analyzed. The proposed reaction mechanisms are described and critically discussed. Points of convergence and of disagreement are underlined. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Selective catalytic reduction; NO<sub>x</sub> removal; Mechanism of SCR

## 1. Introduction

The acid rains and the town smog, produced mainly by atmospheric pollutants like SO<sub>x</sub>, NO<sub>x</sub> and volatile organic compounds, are among the most serious world ecological problems since they cause irreversible changes in the terrestrial and aquatic ecosystems [1]. In recent years, great efforts have been applied to limit the emission of such pollutants through the widespread application of available methods and/or via the development of new technologies [2–4].

In the case of nitrogen oxide emissions, most of NO<sub>x</sub> are produced during the combustion processes (*thermal* NO<sub>x</sub>) by the oxidation of the atmospheric nitrogen at very high temperatures:



NO<sub>x</sub> typically consists of a mixture of 95% NO and 5% NO<sub>2</sub>. Other NO<sub>x</sub> are formed by oxidation of the organic nitrogen present in the fuel (*fuel* NO<sub>x</sub>) and from HCN formed from fuel nitrogen (*prompt* NO<sub>x</sub>) [1–4]. Many efforts have been made to minimize NO<sub>x</sub> emission (DeNO<sub>x</sub>ing) either by combustion control or by post-combustion abatement technologies. Combustion control is achieved by the use of

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low  $\text{NO}_x$  burners, flue gas recirculation, fuel reburning, staged combustion and water or steam injection [2–5]. Post-combustion DeNOxing [2–4,6] includes wet methods, as sorption (their use is not of commercial importance because of the high costs) and dry methods, such as catalytic (heterogeneous) or homogeneous reduction.

Catalytic technologies [7–11] are attractive because of their low cost and high efficiency. In principle, the simple NO decomposition (the reverse of reaction (1)) is a thermodynamically favored reaction at low temperatures and could be applied. However, the reaction is very slow and sufficiently efficient catalysts have not been discovered so far. Consequently, to convert NO into  $\text{N}_2$  a reducing agent must be used. In the case of the catalytic converters of cars [10,11], CO acts as the actual reducing agent for NO. The  $\text{NO}_x$  reduction is achieved using Pt–Rh or Pd-based catalysts deposited on alumina coatings or washcoats on ceramic monoliths [11]. Alternatively, hydrocarbons such as methane, propane or propene can be used as reductants. However, also for these reactions no sufficiently active catalysts have yet been found [8,9].

DeNOxing of waste gases from stationary sources can be efficiently achieved by using the so-called SCR (selective catalytic reduction) process [6,12–14]. Nowadays, the large majority of the current industrial DeNOxing is carried out by this technology. In this case ammonia injected in the waste gases is used as the reducing agent. This technology has been first developed in Japan in the 1970s and is widely applied worldwide today. However, many chemical aspects of this technology are still object of discussion in the scientific literature. In particular, the reaction mechanism is still not unanimously recognized. On the other hand, we believe that the extensive research activities carried out in many laboratories could lead, in principle, to substantial agreement on several mechanistic details. We will summarize here the literature data on this topic and we will try to identify points of agreement and of debate.

## 2. Metal oxide catalysts for the SCR process

The industrial catalysts for the SCR process are based on  $\text{TiO}_2$ -supported  $\text{V}_2\text{O}_5$ – $\text{WO}_3$  and/or  $\text{V}_2\text{O}_5$ – $\text{MoO}_3$  oxides [6,12–15]. However, a number of other

formulations have been reported to be active and more or less selective for this reaction. Bosch and Janssen [12] in their review published in 1988 reported a very extensive survey of catalysts formulations found active until then. Among metal oxides, pure vanadia and vanadia supported on oxides carriers such as alumina, silica, zirconia and titania (which is the choice support nowadays) have been deeply investigated. Additionally, catalysts based on pure, supported and/or mixed iron [16–19], copper [19–22], chromium [18,23–25] and manganese oxides [26,27] also underwent wide application and testing in the scientific literature. The same transition metals have been also introduced into zeolitic cavities, such as in the cases of X, Y and ZSM5 cation exchanged zeolites [12,21,28,29], and have been added to  $\text{TiO}_2$ -pillared clays [30].

A broad overview of these data shows that every metal oxide which is active in oxidation catalysis can act as an active component in the SCR reaction. Catalyst components which give rise to high selectivity in partial oxidation ( $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$  and  $\text{MoO}_3$ ) when supported on  $\text{TiO}_2$  give also rise to high selectivity in the SCR reaction. Transition metal oxides which are poorly active in oxidation catalysis (such as  $\text{TiO}_2$  and  $\text{ZrO}_2$ ) are also poorly active in SCR catalysis. This is in line with the evidences showing that the SCR reaction is a redox process that occurs with a redox or Mars-van Krevelen-type mechanism (see below).

## 3. The active phase and the role of the support and of promoters in the industrial catalysts

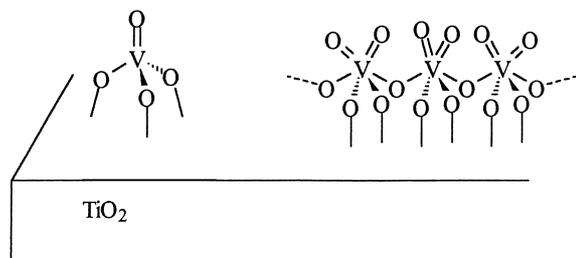
Several studies have been published concerning the characterization of  $\text{V}_2\text{O}_5$ – $\text{WO}_3/\text{TiO}_2$  model [31–37] and industrial [15] SCR catalysts. On the other hand, less data are known on  $\text{V}_2\text{O}_5$ – $\text{MoO}_3/\text{TiO}_2$  catalysts [38–40]. In all cases it has been found that the best catalysts contain just a few less than a full “monolayer” of vanadium plus tungsten (or molybdenum) oxides over the  $\text{TiO}_2$ -anatase support. The amount of vanadium oxide is variable but generally very small (<1% (w/w)), at least in the most recent catalyst formulations [15]. Indeed vanadia is responsible for the activity of the catalyst in the  $\text{NO}_x$  reduction but also for the undesired oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the case of sulfur bearing fuels.  $\text{WO}_3$  is employed in larger

amounts ( $\approx 10\%$  (w/w)) to increase the catalyst activity and thermal stability [14,33].

The choice of  $\text{TiO}_2$ -anatase as the best support for SCR catalysts relies on two main reasons:

1.  $\text{SO}_2$  is usually present in the waste gases of power plants and in the presence of oxygen it can be oxidized to  $\text{SO}_3$  thus forming metal sulfates by reacting with the oxide catalyst supports.  $\text{TiO}_2$  is only weakly and reversibly sulfated in conditions approaching those of the SCR reaction and the stability of sulfates [15,41] on the  $\text{TiO}_2$  surface is weaker than on other oxides such as  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  [42]. Consequently,  $\text{TiO}_2$ -based industrial catalysts are only partially and reversibly sulfated at their surface upon SCR reaction in the presence of  $\text{SO}_2$ , and this sulfation even enhances the SCR catalytic activity [43].
2. It is ascertained that supporting vanadium oxides on  $\text{TiO}_2$ -anatase leads to very active oxidation catalysts, more active than those obtained with other supports. This has also been found for  $\text{V}_2\text{O}_5$ - $\text{TiO}_2$  (anatase) “monolayer” type catalysts for the selective oxidation of ortho-xylene to phthalic anhydride [44,45]. The reason for this activity enhancement can be found on the good dispersion of vanadium oxide on  $\text{TiO}_2$  giving rise to “isolated” vanadyl centers and “polymeric” polyvanadate species [46–50], possibly of the metavanadate-type [51] (Scheme 1), and also on the semiconductor nature of  $\text{TiO}_2$ , whose conduction band is not very far from the d-orbital levels of vanadyl centers, located in the energy gap [37].

Accordingly,  $\text{TiO}_2$ -anatase is an “activating” support, giving rise to catalysts that are stable against sulfation or even improved upon sulfation.



Scheme 1. Proposed structures for monomeric vanadyl species [46–49] and polymeric metavanadate species [51] in their dehydrated forms on the surface of  $\text{V}_2\text{O}_5$ - $\text{TiO}_2$  catalysts.

All authors agree that the active sites on the  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ - $\text{MoO}_3/\text{TiO}_2$  industrial SCR catalysts are vanadium oxide species. In fact W- and Mo-free  $\text{V}_2\text{O}_5/\text{TiO}_2$  is also active and quite selective in SCR, its activity being definitely better than those of  $\text{WO}_3/\text{TiO}_2$  and  $\text{MoO}_3/\text{TiO}_2$  [12,14,33,50,52]. However, it has been found that  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  is both more active and more selective than  $\text{V}_2\text{O}_5/\text{TiO}_2$  (see [12,14,33,52,53,49](c)). In Fig. 1 the conversion of NO measured on different catalysts belonging to the  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  system is reported. It clearly appears that (i) the activity of the catalysts is increased by increasing the V loading, and (ii) the addition of  $\text{WO}_3$  increases the activity of  $\text{V}_2\text{O}_5/\text{TiO}_2$ . According to Orlik et al. [52] and Spitznagel et al. [54],  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  catalysts are more active, in As-free atmosphere, than  $\text{V}_2\text{O}_5$ - $\text{MoO}_3/\text{TiO}_2$ .

It is worth to note that  $\text{V}_2\text{O}_5/\text{TiO}_2$  (anatase) is quite an unstable system. In fact,  $\text{TiO}_2$ -anatase is a metastable titanium dioxide polymorph and tends to convert into the thermodynamically stable form rutile at any temperature and pressure [55]. The anatase-to-rutile phase transformation is favored by  $\text{V}_2\text{O}_5$  [56,57] which also favors the anatase sintering and loss of surface area [33]. On the contrary,  $\text{WO}_3$  [57–59] and  $\text{MoO}_3$  [60] hinder both surface area loss of anatase and its transformation to rutile. This can be another reason for their addition to vanadia-titania. A further reason may be related to the effect of such components in the undesired  $\text{SO}_2$  oxidation. In fact,  $\text{WO}_3$  and  $\text{MoO}_3$  compete with and displace  $\text{SO}_3$  on the basic sites of the  $\text{TiO}_2$  surface and tend to cover it, thus limiting its sulfation. Accordingly they possibly decrease also the catalytic activity of the SCR catalysts for the  $\text{SO}_2$  to  $\text{SO}_3$  oxidation. It is also noted that  $\text{MoO}_3$  addition has a specific role in the presence of As compounds in the gas, even if the mechanism of this prevention is still largely unclear [61–63].

In conclusion,  $\text{MoO}_3$  and  $\text{WO}_3$  act both as stabilizers and as promoters of the SCR catalysts and possibly as inhibitors of the  $\text{SO}_2$  oxidation.

The mechanism with which tungsten oxide can activate the vanadium oxy-centers for the SCR is still matter of debate. Some authors [64] pointed out that tungsten oxide gives rise to stronger Brønsted acid sites, whose presence favors the reaction. Other authors proposed that the SCR reaction needs two sites, and  $\text{WO}_3$  can offer the presence of a second site

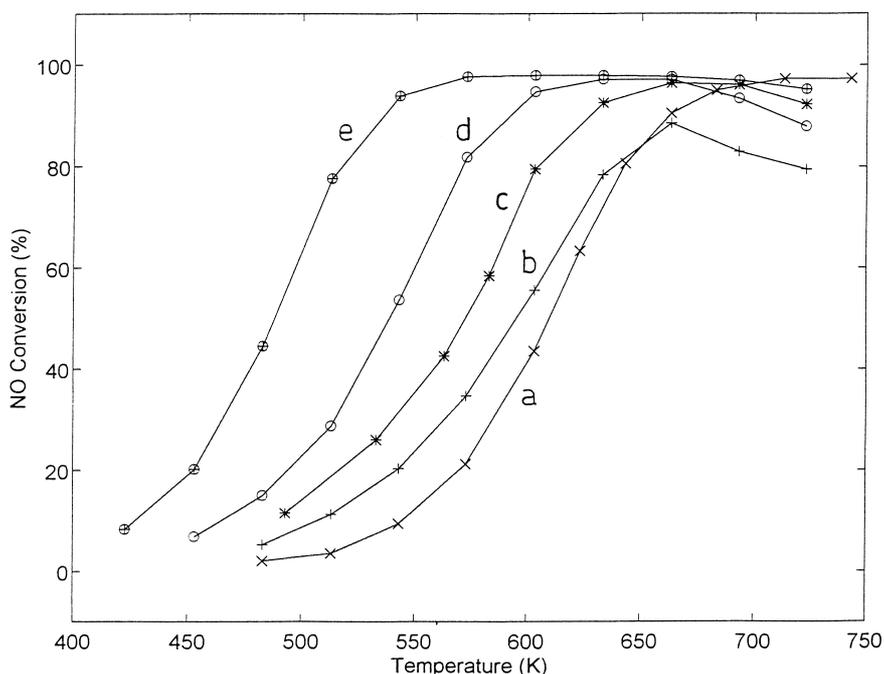


Fig. 1. NO conversion versus temperature over: (a) WO<sub>3</sub>(9)/TiO<sub>2</sub>; (b) V<sub>2</sub>O<sub>5</sub>(0.78)/TiO<sub>2</sub>; (c) V<sub>2</sub>O<sub>5</sub>(1.4)/TiO<sub>2</sub>; (d) V<sub>2</sub>O<sub>5</sub>(0.78)-WO<sub>3</sub>(9)/TiO<sub>2</sub>; (e) V<sub>2</sub>O<sub>5</sub>(1.4)-WO<sub>3</sub>(9)/TiO<sub>2</sub>. Experimental conditions: catalyst weight, 160 mg (60–100 mesh);  $P=1$  atm; flow rate=60 Ncc/min; feed: He+800 ppm NH<sub>3</sub>+800 ppm NO +1% O<sub>2</sub>. Reprinted with permission from [14].

[49](c). These two concepts will be further discussed below. Alternatively, it has been suggested that the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> solid presents quite peculiar electronic features, involving the semiconducting nature of titania and the similarity of the *d* levels of tungsten, vanadium and titanium. In other words, W and V oxide centers, although vibrationally and “chemically isolated”, interact electronically through the TiO<sub>2</sub> conduction band. This would lead to a further enhancement of the activity and selectivity of the reaction sites, which are vanadyl centers [33,37].

Most authors believe that on industrial catalysts belonging to the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> system, with less than 1% of V<sub>2</sub>O<sub>5</sub> (w/w), vanadium oxide species are nearly “isolated” and lie between tungsten oxide species, that are apparently either isolated [58] or more or less polymerized [49](a).

It has been shown that model V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts produced by impregnation are good models of the industrial ones [15]. However, real honeycomb catalysts also contain silicate-based particles (like

small glass balls and bentonite fibers) likely due to their effect in improving the mechanical resistance of the honeycomb. These particles contain alkali and alkali-earth cations. It has been suggested [15] that these cations, poisons of SCR catalysts [65,66], can contaminate the catalyst. This may explain some differences in the surface acidity of real and model samples.

#### 4. The SCR reaction stoichiometry and the by-reactions

After discussions performed in the years before 1980, when it was supposed that the true reactant for the SCR process could be NO<sub>2</sub> [67], it has been clarified that the reaction (2) occurs negligibly under the diluted conditions of waste gases. It has been concluded that nitrogen monoxide NO is the actual reactant in SCR [68] and that oxygen does participate in the reaction [69,70]. Today, all authors agree that

the reaction stoichiometry in typical SCR conditions is the following:

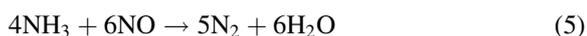


Using isotopically labeled reactants, it has been demonstrated that both on vanadia-based catalysts [71–73] and on noble metals [74], the two nitrogen atoms of  $\text{N}_2$  arise, one from NO and the other from ammonia.

$\text{V}_2\text{O}_5$ -based catalysts also catalyze the reduction of  $\text{NO}_2$  in the presence of oxygen [75,76]:

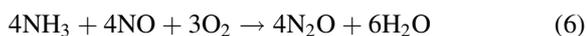


In the absence (or defect) of  $\text{O}_2$  the reaction stoichiometry (3) converts [69,70] into the following:



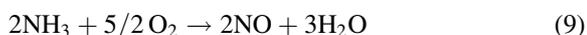
This reaction can be formally considered as the combination of the reverse of reaction (1) plus reaction (3). In this case, four  $\text{N}_2$  molecules arise from a reaction between NO and  $\text{NH}_3$  (through reaction (3)) one arises from two molecules of NO.

The reaction between NO and ammonia can also proceed in a different way, giving rise to the unwanted product  $\text{N}_2\text{O}$ :



In general, authors agree that under typical SCR conditions, with  $\text{NH}_3/\text{NO}$  near 1, few percent oxygen and  $T < 400^\circ\text{C}$ , reaction (3) accounts for the overall stoichiometry on the best catalysts [12–14]. Accordingly, the SCR process occurs when  $\text{N}_2$  is produced with selectivity close to 100% and the ratio of converted moles of NO and  $\text{NH}_3$  is 1.

Unselective behavior occurs when products other than  $\text{N}_2$  (namely  $\text{N}_2\text{O}$ ) are formed (e.g. via reaction (6)) and/or when the ratio of converted NO and  $\text{NH}_3$  moles is lower than 1. This implies that ammonia is converted by ways other than reaction (3), i.e. is in part oxidized by oxygen instead of NO through one of the following ways:



Reaction (7) is now under deep investigation, because in principle it can allow to abate the ammonia

slip after the SCR reactors (if working with excess of ammonia), without introducing other reactant in the gas mixture and without producing further pollutants [77–79]. This is the so-called SCO process (selective catalytic oxidation of ammonia). Several active SCR catalysts are also active in SCO although at slightly higher temperatures.

Reaction (9) is applied industrially in the nitric acid synthesis process [80] using Pt gauzes as the catalysts. However, it has been shown that many transition metal oxides can also catalyze it [81–83]. Upon SCR, reactions (7) and (9) account for an unbalanced conversion of NO and  $\text{NH}_3$  molecules, even in the absence of  $\text{N}_2\text{O}$  among the products.

Reactions (7)–(9) have been shown to occur on most transition metal oxides [81–83], and, in particular, over systems which are active in SCR [77–79,81–86]. In general, reaction (7) is favored with respect to reaction (9) at lower temperatures, while the reverse is found at higher temperatures. Due to the higher thermodynamic stability of  $\text{N}_2$  with respect to NO and  $\text{N}_2\text{O}$ , it is obvious that reactions (8) and (9) must be parallel more than in series with respect to reaction (7). All of them are also parallel to reaction (3), although they can have intermediates in common.

$\text{N}_2\text{O}$  can arise from  $\text{NH}_3 + \text{NO}$  (reaction (6)), from  $\text{NH}_3$  oxidation (reaction (8)) and from NO alone, without participation of ammonia, i.e. through reactions such as:



Reaction (10) can be mediated by the dimeric species of NO, i.e.  $\text{N}_2\text{O}_2$ . It can be an intermediate step in NO decomposition (the reverse of reaction (1)). In fact, transition metal oxide catalysts [87] like those active in the SCR [88] can also be active as catalysts for the decomposition of  $\text{N}_2\text{O}$ :



Reaction (11) is the disproportionation of NO and is a gas-phase reaction, favored at high pressures [89]. As it will be further discussed below, isotopic labeling experiments [71,90] showed that under typical SCR conditions and over SCR metal oxide catalysts, reaction (6) is the main one for  $\text{N}_2\text{O}$  production and reactions (10) and (11) do not occur.

## 5. The catalysts behavior in the $\text{NH}_3 + \text{NO}$ reaction

It is obvious that on SCR catalysts reaction (3) must be faster than the competitive reactions (6)–(9).  $\text{V}_2\text{O}_5\text{--WO}_3\text{--TiO}_2$  catalysts show significant activities for SCR in excess of oxygen already at temperatures near 420 K [12,14,33,53]. In typical SCR conditions NO conversion approaches to be total with converted  $\text{NH}_3/\text{NO}$  ratios of 1 already near 550 K and upon a working window up to 650–700 K (Fig. 1). This behavior implies that reaction (3) occurs selectively and no  $\text{N}_2\text{O}$  is formed in this working window.

However, at temperatures higher than those corresponding to the working window, the NO conversion decreases progressively, as also shown in Fig. 2 [91]. This is due to the onset of reactions (6)–(9) that become competitive with reaction (3) and both subtract the reactant  $\text{NH}_3$  (the case of reactions (7) and

(8)) and/or produce back NO (reaction (9)). When (with feed  $\text{NH}_3/\text{NO}$  ratios  $\approx 1$ ) the NO conversion starts to decrease, in general  $\text{N}_2\text{O}$  appears and the ratio of converted  $\text{NH}_3/\text{NO}$  is higher than 1.

$\text{V}_2\text{O}_5\text{--WO}_3\text{--TiO}_2$  catalysts are also active and selective in the  $\text{NH}_3$  oxidation (reaction (7)), but at temperatures higher than those corresponding to the SCR reaction (3) [12]. Accordingly on industrial catalysts in the working temperature window reaction (3) is faster than reactions (6)–(9). The observation that over SCR catalysts the presence of NO favors  $\text{NH}_3$  consumption via route (3) instead through the competitive reactions (6)–(9) indicates that the SCR reaction and the  $\text{NH}_3$  oxidation reaction involve different rate-determining steps.

The complex chemistry of the SCR systems has also been studied by investigating the ammonia oxidation reaction [77–86,92]. These studies showed that reactions (7)–(9) are actually competitive reactions. In this

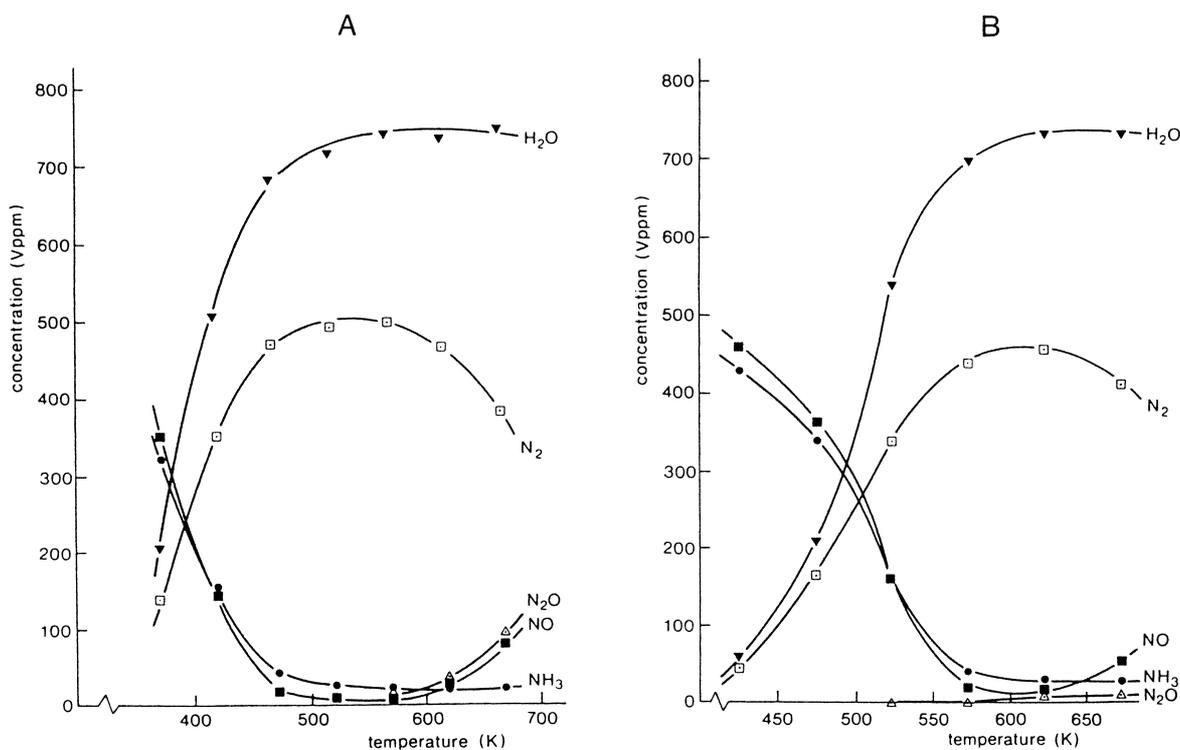


Fig. 2. (A) Concentration profiles of NO,  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  over the  $\text{V}_2\text{O}_5\text{--WO}_3\text{--TiO}_2$  catalyst at a space velocity of  $7.4 \text{ l g}^{-1} \text{ h}^{-1}$ . The inlet concentration of NO and  $\text{NH}_3$  are 500 Vppm; balance He with 2%  $\text{O}_2$ . (B) Concentration profiles of NO,  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  over the  $\text{Fe}_2\text{O}_3\text{--SiO}_2$  catalyst at a space velocity of  $160 \text{ l g}^{-1} \text{ h}^{-1}$ . The inlet concentration of NO and  $\text{NH}_3$  are 500 Vppm; balance He with 2%  $\text{O}_2$ . Reprinted with permission from [91].

case, silica-based catalysts appear to be more active than titania-based catalysts, while selectivity to  $N_2$  is much better on  $MoO_3-SiO_2$  and on  $V_2O_5-SiO_2$  than on  $MoO_3-TiO_2$  and on  $V_2O_5-TiO_2$  [78]. The reverse is found for silica- and titania-supported tungsta [84]. This shows that the chemistry and likely the structure of the actual catalyst site is strongly influenced by the support. As a matter of fact, Biermann et al. [77] showed that on  $MoO_3-SiO_2$  catalysts with high molybdena content reaction (7) is definitely faster than reaction (3), which almost does not occur. This contrasts with the behavior of typical SCR catalysts where reaction (7) competes with reaction (3) only at high temperatures.

Parallel behaviors, with a temperature range with maximum NO conversion upon SCR and the competition of SCR and ammonia oxidation reactions, have been found on any vanadia-based catalyst, like for  $V_2O_5-ZrO_2$  catalysts [93]. However, very similar behavior has also been reported for catalysts with very different formulations. In Fig. 2, a comparison is shown between the behavior of a  $V_2O_5-WO_3-TiO_2$  catalyst and a  $Fe_2O_3-SiO_2$  catalyst [91]. Again, this behavior can be found for supported CuO-based catalysts [12,21,94,95], as shown in Fig. 3.

The same features have been reported on catalysts with different active cations [12] like, e.g. on Mn-based catalysts ( $MnO_x-Al_2O_3$ ,  $MnO_x-WO_3-Al_2O_3$  [26,96] and  $MnO_x-TiO_2$  [79]), on a number of Cu-

based catalysts [12,94,95] including CuO-carbon [96], and CuO-MgO- $Al_2O_3$  [22,97], and on  $Fe_2O_3$ -based [16–19,91] and  $Cr_2O_3$ -based [16,18,23–25,98] catalysts. However, in these cases the maximum conversion obtained is frequently lower than on industrial catalysts at a given temperature, the working window for the SCR is smaller, the selectivity to nitrogen is lower than 1 with significant  $N_2O$  production also at low temperature, and the ratio of converted  $NH_3$  and NO is frequently higher than 1. This implies that Cu-, Fe-, Cr- and Mn-based oxides efficiently catalyze reactions (6)–(9), so that they are less selective than  $V_2O_5$ -based catalysts. In any case, the observed parallelism in the catalytic behavior of these catalysts suggests that the basic mechanistic features of the reactions on these different metal oxide samples should be the same. This is in line with the observation that in oxidation catalysis the basic mechanistic features are usually mainly determined by the chemistry of the reactants [99].

## 6. The observed reaction kinetics

Several kinetic studies, mostly obtained under “real” conditions, have been reported for the SCR reaction. These are based on both merely empirical expressions (e.g. power-law kinetics) and/or mechanistic approaches (e.g. Langmuir–Hinshelwood or

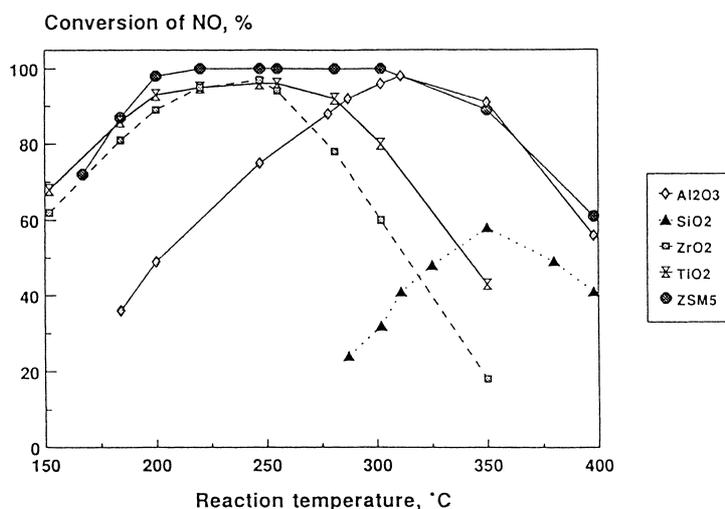


Fig. 3. Comparison of the conversion of NO in copper samples (%wt CuO) on various oxide supports. Reprinted with permission from [95].

Eley–Rideal models). A detailed survey of the kinetic models developed for the SCR reaction is outside the aim of the present review. However, since several authors deduced mechanistic information from their kinetic models, in the following such results will be briefly discussed.

The NO conversion rate for the SCR process can be supposed to depend on the concentrations of the reactants  $C_{\text{NO}}$ ,  $C_{\text{NH}_3}$  and  $C_{\text{O}_2}$ , and also from the concentration of water,  $C_{\text{H}_2\text{O}}$ , which is a reaction product and is also present in the feed under actual SCR conditions. Accordingly, the following empirical power kinetic equation can be used to model kinetic data:

$$r_{\text{NO}} = k_c C_{\text{NO}}^\alpha C_{\text{NH}_3}^\beta C_{\text{O}_2}^\gamma C_{\text{H}_2\text{O}}^\delta \quad (13)$$

The reaction order with respect to NO,  $\alpha$ , has been measured by many authors to be 1 on vanadia-based catalysts (see [43](a) and [52,68,100–105]). However, other authors measured lower  $\alpha$  values, in the range 0.5–0.8 [106–109]. Odenbrand et al. [107] and Linz and Turek [108] found it to increase by increasing reaction temperature.

A reaction order on NO of 1 has also been found on  $\text{Cr}_2\text{O}_3/\text{TiO}_2$  [25], on Fe-Y zeolite [28] and on Cu-ZSM5 [29] and other Cu-exchanged zeolites [29,110]. Komatsu [111] measured a value of 0.8 on Fe-ZSM5, Willey et al. [18] measured  $\alpha=0.64$  on ferric oxide while Singoredjo and coworkers [26,96] found on  $\text{MnO}_x\text{-WO}_3\text{-Al}_2\text{O}_3$  a reaction order with respect to NO even lower, namely 0.4.

Working in excess of oxygen and in the absence of water vapor or with water contents above 5%, the rate dependencies from oxygen and water can be neglected. Under these conditions, according to Inomata et al. [68] (for pure  $\text{V}_2\text{O}_5$ ) and to Wong and Nobe [100] (for  $\text{V}_2\text{O}_5/\text{TiO}_2$ ), working with  $\text{NH}_3/\text{NO} \geq 1$  Eq. (13) reduces to

$$r_{\text{NO}} = k_c C_{\text{NO}}, \quad (14)$$

which means that the reaction order with respect to ammonia,  $\beta$ , is 0. According to Orlik et al. [52] working on monolithic 15%  $\text{V}_2\text{O}_5\text{-TiO}_2$  the reaction rate is first order in ammonia at very low  $C_{\text{NH}_3}$  and becomes zero order when stoichiometry for reaction (5) (i.e. the direct reaction of  $\text{NO}+\text{NH}_3$  without participation of oxygen) is attained. No effect of ammonia concentration on the reaction rate has been

reported by several other authors on vanadia-based catalysts [102–105]. Eq. (14) has been successfully used to model SCR monolith reactors working in excess of  $\text{NH}_3$  [112].

According to some authors, working with a sub-stoichiometric  $\text{NH}_3/\text{NO}$  ratio (as actually occurs in industrial reactors to minimize ammonia slip) the rate dependence from  $C_{\text{NH}_3}$  appears. In this case,  $\beta$  values near 0.2 have been measured [107–109].

Zero order with respect to ammonia has also been measured on Cu-ZSM5 [29] and on Fe-ZSM5 [111] zeolites. According to Singoredjo and coworkers [26,96] the reaction order with respect to ammonia on  $\text{MnO}_x\text{-WO}_3\text{-Al}_2\text{O}_3$  is slightly negative at 383 K and is slightly positive at 423 K. These authors proposed that NO adsorbs on a different site than ammonia, but that ammonia can also compete with NO on its adsorption sites. Also Willey et al. [18] and Amiridis et al. [28] found, on ferric oxide and on Fe-Y-zeolite catalysts, respectively, a slight inhibiting effect of ammonia ( $\beta < 0$ ).

Conflicting data are reported on the reaction order with respect to oxygen, generally found in the range 0–0.5 [103–105,111], which has however been neglected by many authors because, in practical conditions, oxygen is in large excess. In any case, most authors agree that oxygen is involved in the reoxidation of the catalyst in a Mars-van Krevelen or “redox” type mechanism. If this is true, dioxygen does interact with neither NO nor  $\text{NH}_3$ , and this is also an important indication for the details of the reaction mechanism. Some authors, like Marshneva et al. [34] and Lietti et al. [53] for  $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$  catalysts and Cizek [113] for  $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$ , concluded that the slow step of the SCR reaction is or can be associated to the catalyst oxidation step by oxygen.

Water is a product of the SCR reaction, and interacts strongly with the surface of the catalysts, modifying the structure of the active sites [46–49] and possibly allowing the retention of high oxidation state [114]. All authors, with few exceptions [56], agree that water hinders the SCR reaction [106–109,115,116] (negative value of  $\delta$ ) although this effect is no more evident, on industrial catalysts, for  $\text{H}_2\text{O}$  levels above 5% (v/v) [14]. The inhibiting effect of water has been interpreted as an effect of a competition of  $\text{H}_2\text{O}$  with  $\text{NH}_3$  on the reaction sites. Interestingly, most authors agree that water improves selectivity (i.e. reduces  $\text{N}_2\text{O}$

formation) on  $V_2O_5/TiO_2$  catalysts [109,115,116], which means that  $H_2O$  affects reactions (6) and/or (8) more than reaction (3).

In conclusion, different pictures arise from the kinetic analysis of the SCR reaction on different catalysts and in different conditions. However, as discussed above, on many catalysts surfaces and in many practical conditions, the kinetics of SCR can be modeled with a simple power-law kinetics (Eq. (14)) with first order in NO, zero order in ammonia, oxygen and water. This is valid on vanadia-based catalysts (in particular, at high temperature) as well as on Cu-zeolites.

The above mentioned kinetic results have been interpreted in different ways:

1. As first concluded by Inomata et al. [68] and later agreed by most authors on vanadia-based catalysts [12,71,117], the observed reaction order should indicate that ammonia reacts from a strongly adsorbed state while NO reacts from the gaseous or a weakly adsorbed state;
2. As suggested by Komatsu et al. [29,111] for metal-exchanged zeolites, the rate-determining step can be the adsorption of NO, supposed by these authors to occur together with oxygen to give an oxidized adsorbed species.

Obviously, these two quite different interpretations of the same kinetic laws are based on results arising from different and complementary measurements, e.g. spectroscopic adsorption studies and thermodesorption investigations (see below).

In several cases the NO reaction order lower than 1 (e.g. in the range 0.4–0.7) has been interpreted by supposing that NO adsorbs (either on the same site as ammonia [18] or on a different site [26,96]) and reacts from the adsorbed state with adsorbed ammonia. However, this is not the only possible reason for a reaction order lower than 1. As shown by Dumesic et al. [117] and by Busca and Ramis [118], this can also reflect the existence of a slow step for ammonia activation. According to Tufano and Turco [109] another possible reason can be due to a slow step after formation of a complex between NO and ammonia, or to the competitive adsorption of water (a reaction product) with ammonia on the same site. The slight inhibiting effect of ammonia, observed in some cases, is interpreted on the basis of a competition of  $NH_3$  on the NO adsorption sites [18,26,96].

## 7. Adsorption and desorption studies

As discussed above, kinetic data strongly suggest that on all active catalysts ammonia reacts from a strongly adsorbed state, whereas different opinions are available concerning the interaction of NO with the catalytic surface. To elucidate such aspects, the adsorption characteristics of the SCR reactants over various oxide-based catalysts have been extensively investigated, as reported below. Almost the totality of these studies makes use of the usual spectroscopic and/or thermal desorption techniques, and refer to “model” catalysts and “clean” conditions, e.g. catalysts with compositions very far from those of commercial samples, absence of water vapor and  $SO_x$  in the gas stream, vacuum conditions, etc. Accordingly, care must be taken when extrapolating these data for mechanistic purposes to commercial catalysts operating under actual working conditions.

### 7.1. $NH_3$ adsorption and desorption

#### 7.1.1. $V_2O_5$ -based catalysts

The adsorption–desorption characteristics of ammonia on  $V_2O_5$ -based catalysts have been extensively investigated in the literature by means of TPD, FTIR and combined TPD-FTIR techniques. The transient response method has also been applied.

All authors agree in indicating that ammonia adsorbs on pure  $V_2O_5$ , on  $V_2O_5-TiO_2$ , on  $V_2O_5/SiO_2-TiO_2$ , on  $V_2O_5-WO_3/TiO_2$  and on  $V_2O_5-MoO_3/TiO_2$  in two different strongly held species. As shown in Fig. 4 these species are well identified by IR spectroscopies [36,46,50,119–129]. They are: (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 [126] have also been reported to exist. However, this last species is certainly weakly held, so that it is not supposed to be active in the SCR process. Molecular adsorbed  $NH_3$  species are produced on both  $Ti^{4+}$ , vanadyl and wolframyl cations and cannot be distinguished spectroscopically.  $^{15}N$ -NMR experiments allowed to conclude that adsorption on Lewis sites is predomi-

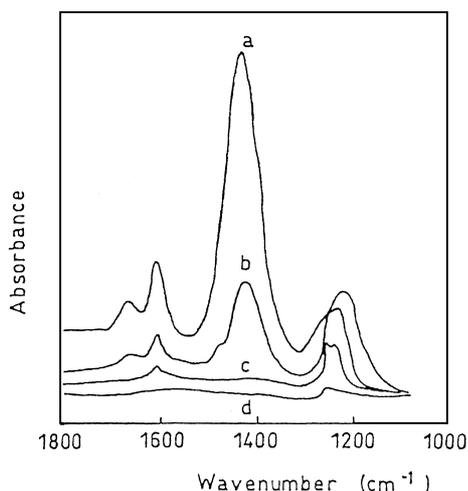


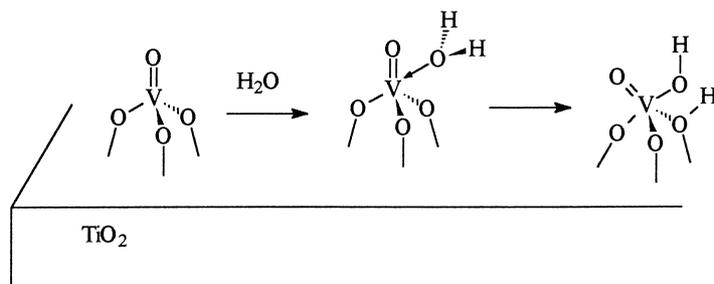
Fig. 4. FT-IR spectra of the adsorbed species arising from adsorption of ammonia over a  $V_2O_5$ - $WO_3$ - $TiO_2$  sample ( $WO_3=9\%$  (w/w) and  $V_2O_5=1.47\%$  (w/w)) and subsequent outgassing at RT (a), 400 K (b), 523 K (c), and 623 K (d). The spectra of the activated catalyst have been subtracted. Reprinted with permission from [133].

nant in  $V_2O_5$ - $TiO_2$  [130]. The  $TiO_2$ -anatase supports, if pure, only shows Lewis acidity [131], whereas ammonium ions are formed on V-OH sites. These data suggest that vanadyl sites are Lewis acidic and can convert into Brønsted sites by water adsorption (Scheme 2):

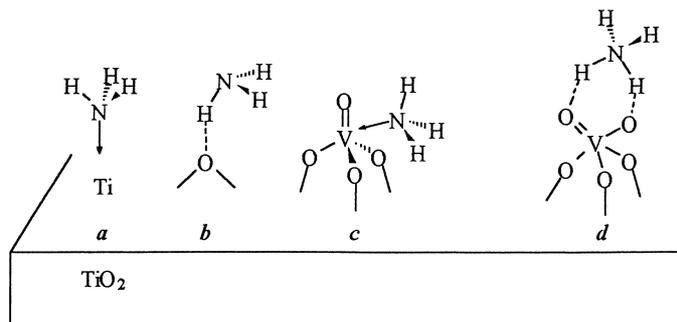
The thermal species arising from ammonia adsorption can be depicted as follows, supposing that polymeric vanadates, coordinatively saturated, do not adsorb ammonia (Scheme 3).

In the case of  $V_2O_5$ - $WO_3$ - $TiO_2$  [15,36,132,133] and on  $V_2O_5$ - $MoO_3$ - $TiO_2$  [134], like on  $WO_3$ - $TiO_2$  [36,132] and on  $MoO_3$ - $TiO_2$  [135] catalysts, Lewis bonded species on wolframyl or molybdenyl species and Brønsted-bonded  $NH_4^+$  species at W-OH sites and Mo-OH are also formed.

The thermal stability of  $NH_3$  adsorbed species has also been investigated by FTIR: it has been found that Lewis bonded molecular species are thermally more stable than ammonium ions (Fig. 4) [122]. It has also been reported that water competes with ammonia on



Scheme 2. Schemes of the generation of the Brønsted acid sites from surface vanadyl centers.



Scheme 3. Proposed structures 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.

Lewis acid sites, whereas it causes an enhancement of the amount of Brønsted acid sites, as deduced from the increased amount of protonated ammonia species [123,124]. However ammonia displaces water from Lewis acid sites, due to its greater basicity. As it will be discussed later, authors debate on if protonated or coordinated ammonia species are those active in the SCR process on vanadia/titania based catalysts. Interestingly, no supports from spectroscopic measurements have been derived to the presence of other  $\text{NH}_3$ -derived species like  $\text{NH}_2\text{O}-\text{V}$  (formally, a dissociated form of hydroxylamine,  $\text{NH}_2\text{OH}$ ) and  $\text{V}-\text{O}-\text{NH}-\text{NH}-\text{O}-\text{V}$ , that have been suggested by some authors to act as intermediate in the SCR reaction and in the SCO reactions (see below).

The adsorption and desorption of ammonia over  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts has also been investigated by TPD methods by several authors (see [50](b) and [136,137]).  $\text{NH}_3$  strongly adsorbs on pure  $\text{TiO}_2$  and vanadia/titania catalysts, and ammonia surface species having different thermal stability exist on the catalyst surface.  $\text{NH}_3$  adsorption energies in the range 18–26 kcal/mol have been estimated analysis of the TPD spectra [136]. The data indicate that at the temperatures typical of the SCR process a significant part of ammonia is adsorbed on the catalyst surface. Similar results have been obtained over  $\text{V}_2\text{O}_5-\text{WO}_3/\text{TiO}_2$  model catalysts [36,138]. Both the amounts and the strength of adsorption decreases upon addition of  $\text{V}_2\text{O}_5$ , thus indicating that the V component decreases the catalyst surface acidity.

The oxidation of a small fraction of adsorbed ammonia to  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}$  has also been reported to occur at high temperatures during TPD experiments over vanadia/titania catalysts (see [50](b) and [137–139]). This oxidation process may involve either lattice oxygen atoms or traces of gaseous oxygen present in the carrier gas stream [137,138], and has been related to the presence of the V components. ESR and XPS data also showed that  $\text{NH}_3$  can reduce the vanadia sites over  $\text{V}_2\text{O}_5/\text{TiO}_2$  [140] while conductance measurements [141] showed that ammonia adsorption caused a significant increase in the conductance of  $\text{V}_2\text{O}_5/\text{SiO}_2-\text{TiO}_2$  catalysts, so confirming a catalyst reduction by ammonia, in agreement with TPR data [142].

Although ammonia oxidation by the oxidized vanadia-based surfaces certainly can occur, the identifica-

tion of the surface species produced by ammonia oxidation is still incomplete and partly tentative. On pure vanadia and on vanadia/titania samples, according to Miyata et al. [121] and Ramis et al. [123,129], spectroscopic features that can be assigned to an amide species,  $-\text{NH}_2$ , are observed. Similar species can be observed on several other active SCR catalysts, see below. These species may act as precursors in the  $\text{NH}_3$  oxidation to  $\text{N}_2$  via their dimeric form, hydrazine  $\text{N}_2\text{H}_4$ , species, as observed on Cu-based catalysts (see below).

The characteristics of  $\text{NH}_3$  adsorption–desorption on model  $\text{V}_2\text{O}_5/\text{TiO}_2$  and  $\text{V}_2\text{O}_5-\text{WO}_3/\text{TiO}_2$  SCR catalysts have been recently investigated by means of the transient response methods [143,144]. In line with the existence of several  $\text{NH}_3$  adsorption states, it has been found that a simple Langmuir approach could not represent the  $\text{NH}_3$  adsorption–desorption data accurately. A nice fit of the data could be obtained by assuming a non-activated  $\text{NH}_3$  adsorption and a Temkin-type desorption kinetics. Values of the activation energy for desorption in the range 18–26 kcal/mol have been estimated for the  $\text{V}_2\text{O}_5/\text{TiO}_2$  sample, in excellent agreement with those reported in [136].

#### 7.1.2. Other oxide catalysts

The  $\text{NH}_3$  adsorption has been investigated also over other active SCR catalysts, like  $\text{CuO}/\text{TiO}_2$  [19,129],  $\text{CuO}-\text{MgO}/\text{Al}_2\text{O}_3$  [97],  $\text{Fe}_2\text{O}_3$  [18,19,145],  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  [146],  $\text{MnO}_x/\text{TiO}_2$  [146],  $\text{MgO}-\text{Fe}_2\text{O}_3$  [19]. Over these catalysts ammonia adsorbs only in a coordinative way at room or lower temperatures (see Fig. 5 for  $\text{CuO}-\text{TiO}_2$ ). Brønsted acidity cannot be found over these surfaces, some of which display a relevant basic character [97]. Also, manganese sites on  $\text{MnO}_x/\text{Al}_2\text{O}_3$  do not seem to be associated to Brønsted acidity [26].  $\text{Cr}_2\text{O}_3$ -based catalysts and  $\text{MnO}_x/\text{TiO}_2$  catalysts, also active in the SCR reaction, show weak Brønsted acidity [18,23–25,146,147]. In Figs. 2 and 3 the catalytic behavior of catalysts displaying Brønsted acidity (those based on vanadia) and free from Brønsted acidity (those based on  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ ) are compared. It is observed that both class of catalysts are active in the reduction of  $\text{NO}$  by  $\text{NH}_3$ . From these data it has been concluded that the existence of Brønsted acidity is not a requisite for the SCR activity at low temperatures [19,129,146].

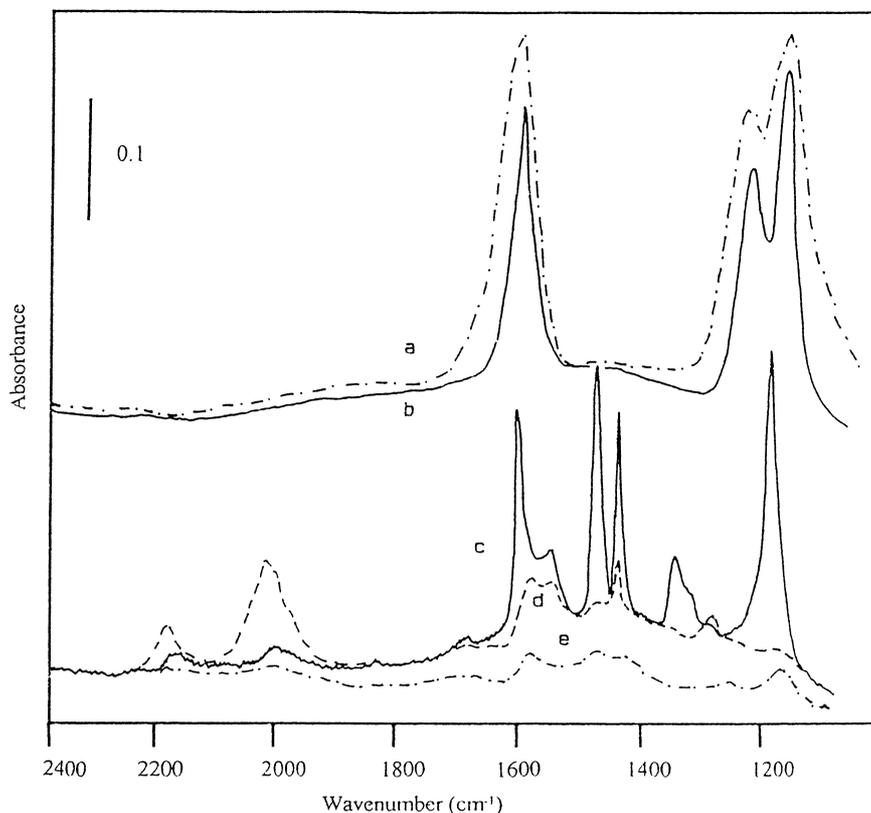


Fig. 5. FT-IR spectra of the adsorbed species arising from  $\text{NH}_3$  adsorption (20 torr) over  $\text{CuO-TiO}_2$  at (a) r.t. and subsequent outgassing at (b) 373 K, (c) 423 K, (d) 523 K, and (e) 623 K. Reprinted with permission from [19].

Lewis bonded and Brønsted bonded ammonia species have also been found on  $\text{Cu-ZSM5}$ , even if over-exchanged [29,148], as well as on other  $\text{Cu-zeolite}$  systems [29,84] and on  $\text{Fe-Y}$  [29] and  $\text{Fe-ZSM5}$  zeolites [111]. In these cases it has been supposed that the Brønsted acid sites are residual non-exchanged OHs of the zeolite, that are retained in spite of the cation over-exchange.

An interesting case is that of  $\text{TiO}_2$ , that, if pure, only shows Lewis acidity and poor catalytic activity for SCR. However, when sulfated, strong Brønsted acidity is formed [131] and SCR activity is strongly enhanced [41], although only at very high temperature. From this and other data (see below) it has been proposed that Brønsted acidity plays an important role in the SCR reaction [41]. However, it should be noted that sulfation also increases the acid strength of the Lewis sites of titania [131,149].

## 7.2. $\text{NO}$ adsorption and desorption

### 7.2.1. $\text{V}_2\text{O}_5$ -based catalysts

The adsorption of the other SCR reactant, i.e.  $\text{NO}$ , has also been extensively investigated in the literature over  $\text{V}_2\text{O}_5$ -based catalysts and over other catalytic systems active in the SCR reaction. The data in this case are however not as clear as in the case of ammonia, since the chemistry of nitrogen oxide at the interface of oxide materials is very complex [150–155]. In principle,  $\text{NO}$  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 can be oxidized by oxide surfaces, giving rise to species like nitrosonium ion ( $\text{NO}^+$ ), nitrite ions ( $\text{NO}_2^-$ ), adsorbed nitrogen dioxide ( $\text{NO}_2$ ), nitronium ion, ( $\text{NO}_2^+$ ), and nitrate ions ( $\text{NO}_3^-$ ). However, it can also act as an oxidizing agent,

reducing itself to  $\text{NO}^-$  and to its dimeric form, the hyponitrite anion ( $\text{N}_2\text{O}_2^{2-}$ ), as well as to  $\text{N}_2\text{O}$  and  $\text{N}_2$ . Moreover, it can dimerize to dinitrogen dioxide  $\text{N}_2\text{O}_2$  (which is possibly an intermediate in its reduction and/or in its oxidation) and to disproportionate giving rise to both reduced and oxidized species.

It has been shown that over catalysts like pure  $\text{V}_2\text{O}_5$  [123,139], on  $\text{V}_2\text{O}_5\text{-TiO}_2$  [123,136–138,156,157],  $\text{V}_2\text{O}_5\text{-SiO}_2$  [156], on  $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$  [156], on  $\text{V}_2\text{O}_5\text{-TiO}_2\text{-SiO}_2$  [141], on  $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$  [138] and on  $\text{V}_2\text{O}_5\text{-MoO}_3\text{-TiO}_2$  [134], the interaction of NO is very weak. Upon contacting a  $\text{V}_2\text{O}_5\text{-TiO}_2$  sample with NO, Ramis et al. [123] observed the formation of a surface nitrosyl species, coordinated to  $\text{Ti}^{4+}$  sites. On the other hand, NO does not adsorb on an ammonia-covered surface since  $\text{NH}_3$  blocks the  $\text{Ti}^{4+}$  adsorption sites due to its greater basicity, and only a minor formation of nitrate species has been observed by nitric oxide oxidation on vanadyl sites. Nitrate and/or nitrite species are observed to form slowly at r.t. and to desorb or decompose easily. A similar behavior has been found on  $\text{V}_2\text{O}_5\text{-ZrO}_2$  [93], where these species have been supposed to take an important role in the SCR reaction.  $\text{NO}_2$  gives more evident adsorbed species on  $\text{V}_2\text{O}_5\text{-TiO}_2$  [123,158].

Conductance measurements showed that NO adsorption causes a slight increase of the conductance of  $\text{V}_2\text{O}_5/\text{SiO}_2\text{-TiO}_2$  catalysts only at high vanadia contents [141], and this has been interpreted as due to a slight catalyst reduction with the production of more oxidized nitrogen oxide species like  $\text{NO}^+$  or  $\text{NO}_2$ . On the other hand, according to Odriozola et al. [139,140], NO is able to reoxidize the centers of reduced  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts and can also adsorb on the  $\text{TiO}_2$  support. In general, most authors today agree on the fact that NO adsorbs as nitrosyl and dinitrosyl surface species on reduced vanadia surfaces, whereas it does not adsorb over fully oxidized surfaces, with few exceptions.

These data show that oxidized NO adsorbed species can be formed at the catalyst surface, although according to many authors NO can also be reduced by reduced catalyst centers. In any case, adsorption is usually negligible at the reaction temperature, particularly in the presence of ammonia. These data allowed some authors to interpret the kinetic data (see above) on vanadia-based catalysts (and in particular the apparent zero and first order kinetics with

respect to  $\text{NH}_3$  and NO, respectively) as due to slow step involving the reaction of gas-phase NO with adsorbed  $\text{NH}_3$ .

Similarly, weak or no adsorption has been found on oxidized supported  $\text{MoO}_3$  and  $\text{WO}_3$ , while quite strong adsorption can occur over these materials after pre-reduction [155].

### 7.2.2. Other oxide catalysts

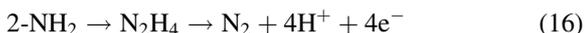
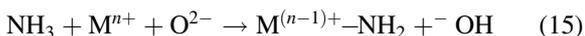
More extensive and stronger adsorption of NO has been found on other active SCR catalysts, like  $\text{Fe}_2\text{O}_3$  [150,153,159–161],  $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$  [18],  $\text{Cr}_2\text{O}_3$  [23,162,163],  $\text{CuO-TiO}_2$  [19],  $\text{CuO/Al}_2\text{O}_3$  [164],  $\text{MnO}_x\text{-Al}_2\text{O}_3$  [27],  $\text{Cr}_2\text{O}_3/\text{TiO}_2$  [98](b). Adsorbed NO has been identified in various forms in these cases, including nitrosyl, nitrate-, nitrite-, hyponitrite- and other anionic species. These species decompose or desorb at relatively low temperatures ( $<250^\circ\text{C}$ ) and mostly gives back NO [96,127]. This behavior can differentiate most metal oxide catalysts from Cu-based zeolites where different adsorbed forms of NO in the presence of oxygen give rise to stepwise desorption during TPD experiments [165]. In this case surface spectroscopy pointed out the existence of the formation of quite stable nitrosyl species together with species that apparently contain more oxygen atoms, whose actual nature is not still completely understood, but that are frequently denoted as  $\text{NO}_2$  or nitrate-like species [148,166,167]. However, also these species decompose giving back mostly NO [21]. Conductance measurements showed that NO adsorption on  $\text{Fe}_2\text{O}_3$  gives rise to both reduced and oxidized species [161]. Recently, a study has been published concerning Ce-mordenite catalysts, reported to be active in SCR [168]. Strong NO adsorption has been found by IR.

### 7.3. Adsorption of other related compounds

To better identify potentially involved surface species, or species revealing mechanistic aspects, the adsorption of other N-containing molecules could be investigated too. With this in mind, the interaction of  $\text{TiO}_2$ ,  $\text{CuO-TiO}_2$  and  $\text{V}_2\text{O}_5\text{-TiO}_2$  with hydrazine ( $\text{NH}_2\text{-NH}_2$ ) and hydroxylamine ( $\text{NH}_2\text{OH}$ ) vapors has also been investigated by IR spectroscopy [19,129,134,146,169]. The spectra of the adsorbed species arising from hydrazine and hydroxylamine

have also been compared with those arising from ammonia on the same surfaces.

In fact, on some surfaces very active in ammonia oxidation, hydrazine ( $\text{H}_2\text{N}-\text{NH}_2$ ) has been identified as an adsorbed species arising from  $\text{NH}_3$  with a quite good degree of certainty [19,129,146], by comparison with the spectrum of hydrazine adsorbed directly from the gas-phase. The catalysts where these species have been observed are  $\text{CuO}-\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3-\text{TiO}_2$ ,  $\text{CrO}_x-\text{TiO}_2$ , and also over-exchanged  $\text{Cu-ZSM5}$  [148]. Previously, a species supposed to be an amide species –  $\text{NH}_2$  was detected on vanadia–titania [121,123]. Similar species can be observed on several other catalysts active in both SCR and ammonia oxidation, such as  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}-\text{Fe}_2\text{O}_3$  catalysts [19,129]. These data, coupled with the known very easy oxy-dehydrogenation of hydrazine in contact with transition metal cations in a high oxidation state, allowed us to propose a mechanism for the surface oxidation of ammonia to nitrogen, that does not disagree with the previous one proposed by Williamson et al. [84] on Cu-zeolites:



The first step involves the activation of ammonia, possibly via the amide species, followed by a coupling reaction that gives rise to nitrogen.

IR studies of the adsorption of hydroxylamine did not confirm the formation of species like  $\text{NH}_2\text{O}-\text{V}$  species (formally a dissociated form of hydroxylamine,  $\text{NH}_2\text{OH}$ ) and  $\text{V}-\text{O}-\text{NH}-\text{NH}-\text{O}-\text{V}$ , which have been supposed by some authors to act as intermediates in the SCR reaction and in the SCO reaction [12,71,73,170]. However such studies supported the identification of a species, detected by oxidation of both ammonia and hydrazine and hydroxylamine, as a nitroxyl species ( $\text{HNO}$ ) [19,146,169]. According to the known chemistry of inorganic nitrogen compounds [171,172] and to some spectroscopic evidences, it can be supposed that the nitroxyl species is the intermediate in the oxidation of ammonia to both  $\text{NO}$  and  $\text{N}_2\text{O}$ .

Another species detectable by IR from ammonia and hydrazine but not from hydroxylamine has been tentatively identified as an imido species ( $\text{NH}$ ). This species could be intermediate in the oxidation of amide to nitroxyl. However, from its behavior it looks quite inactive.

#### 7.4. $\text{NH}_3$ and $\text{NO}$ co-adsorption and surface reaction studies

The data reported above clearly indicate that different species can form on the catalyst surface, that are potentially active in the SCR reaction. In order to obtain more clear indication concerning the nature of the active species (e.g.  $\text{NH}_4^+$  vs. coordinated  $\text{NH}_3$ , gaseous  $\text{NO}$  vs. adsorbed  $\text{NO}$  species) and of the reaction intermediates involved in the reaction, as well as on the nature of the actual catalyst active sites (e.g.  $\text{V}=\text{O}$  sites vs.  $\text{V}-\text{OH}$  sites) and on the sequence of steps of the reaction, spectroscopic (e.g. FTIR and Laser-Raman) and surface reactivity techniques (e.g. temperature programmed reaction studies) have been extensively applied since the 1970s.

Ramis et al. [19,123,132,133] performed co-adsorption and reaction studies in a conventional IR cell while the groups of Topsøe [173] and Baiker [127] performed these studies using an IR flow reactor cell. On the other hand, Wachs [174] reported nice results obtained with a flow reactor Laser-Raman cell. The last three groups denote their studies as *in situ* and accordingly these methods are able, in principle, to detect the surface species (and possibly surface intermediates) while the reaction is occurring. On the other hand, the surface species can also be identified by means of static techniques present upon reaction. In the first case the reactant conversion and the product formation are detected by different analytical techniques (e.g. mass-spectrometry, or FTIR-MS), while in the latter case the disappearance of the reactants and the formation of the reaction products (when IR-active) has been detected by IR. The reliability of *in situ* spectroscopic studies in the detection of reaction intermediates have been briefly discussed elsewhere [99].

Other groups [27,96,127,136–138] make use of the temperature programmed reaction techniques (i.e. TPD, temperature programmed desorption; TPR, temperature programmed reaction and TPSR, temperature programmed surface reaction) to investigate the adsorption, co-adsorption and reaction of adsorbates with gas-phase reactants. Applications of transient reaction methods have also been reported [127,144,164,170], also with labeled molecules [71–73,90].

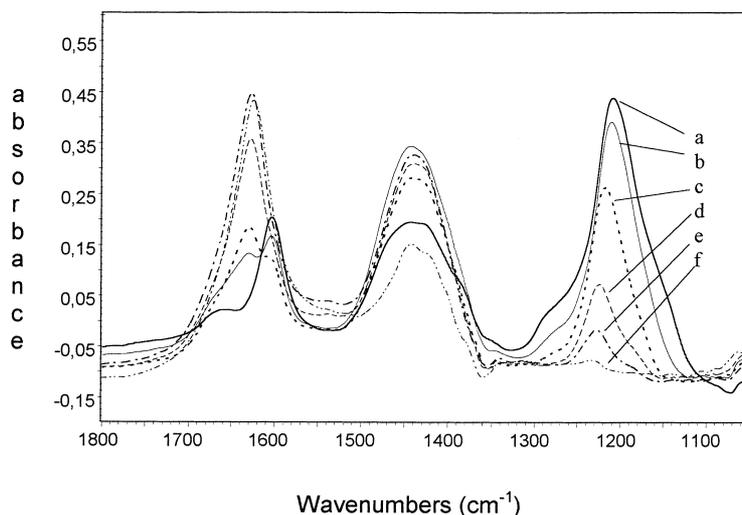


Fig. 6. FT-IR spectra of the adsorbed species arising from the interaction of NO (10 torr) with adsorbed ammonia on a model  $V_2O_5$ - $WO_3$ - $TiO_2$  catalyst, at different temperatures: (a) 300 K; (b) 373 K; (c) 403 K; (d) 423 K; (e) 453 K; (f) 523 K.

It is worth stressing that almost the totality of these studies refers to “model” catalysts and “clean” conditions: accordingly, care must be taken when extrapolating these data to real conditions.

#### 7.4.1. $V_2O_5$ -based catalysts

Detailed FTIR investigations on the co-adsorption of  $NH_3$  with NO on  $V_2O_5/TiO_2$  catalysts has been carried out by Ramis et al. on  $V_2O_5/TiO_2$  catalysts [123] and on  $V_2O_5-WO_3/TiO_2$  catalysts [132,133]. Ammonia has been adsorbed on the surface of the catalysts and then the catalysts have been heated in the presence of NO. The bands corresponding to coordinated ammonia species (ca.  $1200\text{ cm}^{-1}$  in Fig. 6) disappear faster than those of the protonated  $NH_4^+$  species (ca.  $1450\text{ cm}^{-1}$ ), and formation of water (ca.  $1630\text{ cm}^{-1}$ ) has been observed. This contrasts with results obtained upon ammonia adsorption (Fig. 4), during which molecularly adsorbed species were found to be thermally more stable than protonated species. Moreover, the band corresponding to the amide species  $NH_2$  (present in the absence of NO) has not been detected. These results have been explained by considering that a 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  $N_2$  (undetectable by IR). As a matter of facts, IR bands were

also detected that were tentatively assigned to an adsorbed nitrosamide species  $NH_2NO$ , that accordingly has been proposed as an intermediate in the reaction. This has been also supported by the detection of such a molecule among the reaction products by mass-spectrometry [175]. Since no evidence has been derived concerning the presence of NO-derived adsorbed species, an SCR mechanism based on an Eley-Rideal mechanism involving gaseous NO and coordinated  $NH_3$  species has been suggested for the SCR reaction.

Extensive adsorption data of  $NH_3$  in the presence of NO and application of combined in situ FTIR-MS techniques over  $V_2O_5/TiO_2$  catalysts has also been reported by Topsøe et al. [173]. These authors did not analyze the spectral region studied by Ramis et al. [123], that is the most useful to observe the activity of coordinated ammonia (i.e. the region  $1300$ – $1100\text{ cm}^{-1}$ , where only the symmetric deformation of coordinated ammonia falls). In contrast, these authors worked in regions where both coordinated ammonia and the product water absorb (regions of the OH/NH stretching and scissoring modes). They suggested that 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 have been observed on the catalyst surface and this has been taken as an indication that the SCR reaction involves gaseous or weakly adsorbed NO. On the basis of specific experiments performed in the presence and in the absence of oxygen, Topsøe et al. [173] also provided evidence for the presence of a surface redox reaction occurring during the SCR reaction, and proposed an overall reaction mechanism that will be discussed below.

A central role Brønsted-bound ammonia species in the SCR reaction has also been proposed by Schneider et al. [127] on the basis of combined DRIFT-MS experiments performed over vanadia–titania aerogels. These authors observed that the SCR activity correlates with the fraction of Brønsted-bound ammonia species and concluded that the SCR reaction proceeds according to an Eley–Rideal mechanism involving adsorbed  $\text{NH}_3$  species and gas-phase NO.

Surface reactivity studies of pre-adsorbed  $\text{NH}_3$  with gaseous NO over vanadia-based catalysts by means of combined TPSR-MS techniques have been reported by several investigators including the groups of Topsøe [136] and Forzatti [36,137,138]. In these experiments, information on the surface reactivity and on the sequence of the reaction steps have been derived from the analysis of the desorption spectra obtained in inert and/or reactive carriers. On comparing TPD and TPSR data, Srnak et al. [136] observed that in spite of the huge amounts of adsorbed ammonia,  $\text{TiO}_2$  shows poor reactivity in the SCR reaction. The SCR reaction was indeed only monitored in the case of the vanadia/titania samples, in line with the unique role played by V in the SCR reaction. Accordingly a simple relation does not apparently exist between the ability to adsorb  $\text{NH}_3$  and the reactivity in the SCR reaction. By comparing results obtained under vacuum and flow conditions, it is suggested that a key step in the reaction is the activation of the  $\text{NH}_3$  adsorbed species.

The temperature programmed desorption/reaction techniques have also been extensively utilized by Lietti et al. [36,53,137,138,176] in the investigation of mechanistic aspects of the SCR reaction over pure  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2$ ,  $\text{WO}_3/\text{TiO}_2$  and  $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$  catalysts. In particular, the role of gaseous oxygen,  $\text{NH}_3$  coverage, V and W loading on the SCR reaction has been addressed. The authors suggest that 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. These mechanistic data could only be obtained by an appropriate use of the transient techniques that enabled the detection of the detailed sequence of steps of the reaction, as opposite to steady-state methods that, in principle, do not easily allow for such analysis since under steady-state conditions the various steps are progressing at the same rate.

Surface reactivity studies of  $\text{NH}_3\text{+NO}$  mixtures have also been performed by means of transient isotopic labeling experiments performed with  $^{15}\text{NH}_3$ ,  $^{15}\text{NO}$  and  $^{18}\text{O}_2$  under both steady-state and transient conditions [71–73,90]. These experiments significantly contribute in elucidating the source of nitrogen and oxygen in the SCR products over pure and  $\text{TiO}_2$ -supported  $\text{V}_2\text{O}_5$  catalysts, as well as the role of reactions (6)–(9) in the  $\text{NH}_3\text{+NO}$  chemistry. When the  $\text{NH}_3\text{+NO}$  reaction is carried out at relatively low temperatures (usually below 350–400°C) and in the presence of selective catalysts, reaction (3) dominates. In this case, it has been clearly shown by selective labeling of either  $\text{NH}_3$  or NO that of the two N-atoms in  $\text{N}_2$ , one comes from  $\text{NH}_3$  whereas the other is from NO. Accordingly a mechanism that involves the direct coupling of NO and  $\text{NH}_3$  precursors operates in the SCR reaction, thus ruling out the formation of  $\text{N}_2$  from either NO or  $\text{NH}_3$  alone, suggested by Odriozola et al. [139,140]. Along similar lines, it has been shown that formation of  $\text{N}_2\text{O}$  at low temperatures involves one nitrogen atom of  $\text{NH}_3$  and the other from NO, i.e.  $\text{N}_2\text{O}$  formation can be mainly ascribed to reaction (6), whereas at higher temperatures the contribution of reaction (8) may be relevant.

The surface reactivity of model  $\text{V}_2\text{O}_5/\text{TiO}_2$  and  $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$  SCR catalysts has also been recently investigated by means of the transient response methods [143,144]. The data obtained upon adsorption–desorption of the reactants ( $\text{NH}_3$  and NO) confirmed that NO does not appreciably adsorb on the catalyst surface, whereas ammonia is strongly adsorbed (Fig. 7(A)). The  $\text{NH}_3$  adsorption–desorption processes could be nicely fitted by invoking a non-activated adsorption process and a Temkin-type desorption kinetics, with an energy of activation at zero-coverage near 26 kcal/mol. The study of the

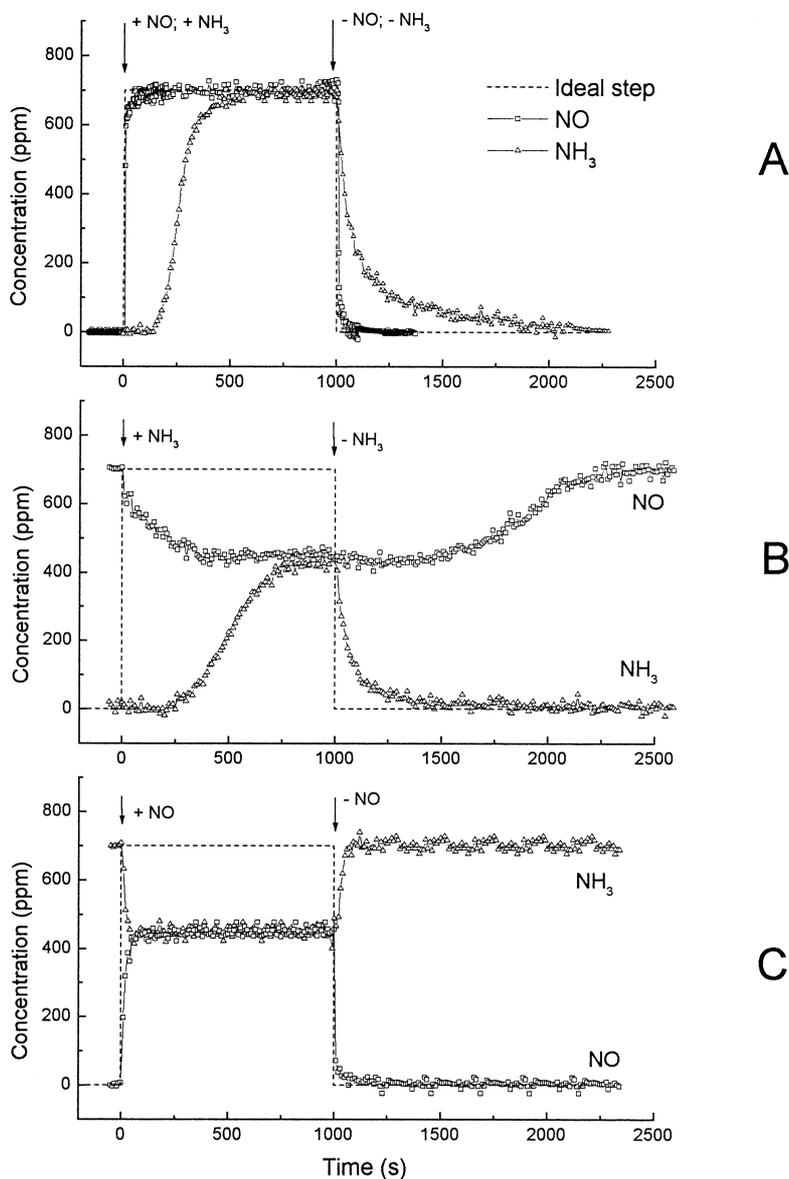


Fig. 7. Results of transient response experiments performed at 493 K over a  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> sample ( $WO_3=9\%$  (w/w) and  $V_2O_5=1.47\%$  (w/w)). Section (A): outlet reactor concentration following a step addition of NO (700 ppm) in He+1% O<sub>2</sub> (squares) and of NH<sub>3</sub> (700 ppm) in He+1% O<sub>2</sub> (triangles). The theoretical inlet step is also reported (dashed line). Section (B): outlet reactor concentrations following a step addition of NH<sub>3</sub> (700 ppm) in He+NO (700 ppm)+O<sub>2</sub> 1%. The N<sub>2</sub> and H<sub>2</sub>O concentrations have not been reported. Section (C): outlet reactor concentrations following a step addition of NO (700 ppm) in He+NH<sub>3</sub> (700 ppm)+O<sub>2</sub> 1%. The N<sub>2</sub> and H<sub>2</sub>O concentrations have not been reported.

dynamic of the SCR reaction (Fig. 7(B) and (C)) showed that: (i) the reaction involves a strongly adsorbed ammonia species and a gaseous or weakly held NO species, in line with the adsorption–desorption

studies of the reactants; (ii) the rate of the DeNO<sub>x</sub> reaction depends on the ammonia surface concentration for NH<sub>3</sub> coverage below a characteristic “critical” value, whereas a much weaker dependence, if

any, exists at high coverage. This is clearly shown in Fig. 7(B) where it is apparent that the NO conversion is not affected for several minutes after the NH<sub>3</sub> shut-off. This suggests that a “reservoir” of adsorbed ammonia species available for the reaction is present on the catalyst surface. The ammonia storage, that 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 adspecies 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 NH<sub>3</sub> over typical SCR catalysts) do not act simply as “spectators” in the SCR reaction but are involved in the NO consumption. We note that one merit of this study was to better clarify the role of the surface sites other than vanadium (i.e. Ti- and W-sites) in the mechanism of the SCR reaction. Such aspects are often neglected in many studies even if it is well known that Ti- and W-sites have a role in the adsorption of ammonia [136].

#### 7.4.2. Other oxide catalysts

Mechanistic studies similar to those reported in the previous section for vanadia-based catalysts have also been performed over other oxide catalysts. In particular, isotopic labeling experiments have been performed over Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [27](b) and Cr<sub>2</sub>O<sub>3</sub> [24]. In line with similar studies performed over V<sub>2</sub>O<sub>5</sub>-based catalyst, also over these oxides both N<sub>2</sub> and N<sub>2</sub>O come from coupling of an NH<sub>3</sub> and an NO molecule. At high temperatures, ammonia oxidation also leads to formation of N<sub>2</sub>O and NO via reactions (8) and (9), respectively.

The reactivity of Mn-supported oxides in the reaction of NH<sub>3</sub> with NO has been extensively investigated by Kapteijn et al. [26,27]. These authors showed that the Mn catalyst does not exhibit Brønsted acidity other than that of the Al<sub>2</sub>O<sub>3</sub>, and accordingly are characterized by a strong molecular interaction with ammonia. Also NO adsorbs on the catalyst surface, giving rise to the formation of NO<sub>2</sub>, nitrito and nitrate groups. Upon NH<sub>3</sub>-NO co-adsorption experiments, the formation of ON-Mn-NH<sub>3</sub> species has been hypothesized to occur.

In the absence of oxygen, a reaction between NH<sub>3</sub> and NO is observed in the IR cell in the temperature range 300–423 K, whereas in the presence of oxygen the reaction is completed already at 325 K. During these experiments, it was shown that the ammonium ion bands remained unaltered, thus showing that these species (associated with the alumina support) do not participate in the reaction.

On the contrary, Schneider et al. [98](b) reported that over Cr<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalysts Brønsted-bound ammonia is involved in the SCR reaction, whereas in the absence of NO direct oxidation of NH<sub>3</sub> to N<sub>2</sub> and N<sub>2</sub>O occurs via a Lewis-bound ammonia species. This has been derived on the basis of transient experiments including temperature programmed desorption (TPD) combined with in situ DRIFT and NH<sub>3</sub> and NO switches during the SCR reaction. The authors also report that the presence of Brønsted-bound ammonia enhances the adsorption of NO, thus favoring the reaction.

Centi et al. [164] performed NH<sub>3</sub>+NO co-adsorption studies as well as pulse and step changes experiments over Cu/Al<sub>2</sub>O<sub>3</sub> catalysts. These authors reported that ammonia adsorbs over this kind of catalysts in the form of chemisorbed and ammonium ions, whereas NO, as opposite to what is typically observed over vanadia-based catalysts, is strongly adsorbed over the catalyst surface. The presence of oxygen enhances NO adsorption in the form of nitrite, nitrate and nitrosyl species. This chemistry has been specifically attributed to the copper surface sites, since the amount of NO adsorbed on the alumina support is very limited. In the presence of ammonia, NO chemisorption is decreased but still evident. FTIR experiments of NH<sub>3</sub>+NO co-adsorption showed a transformation of nitrate species interpreted as due to their reaction to originate ammonium nitrate NH<sub>4</sub>NO<sub>3</sub>. According to these authors, this compound could decompose to gaseous species like N<sub>2</sub>, not detectable by IR, and/or N<sub>2</sub>O. It has however been concluded that this way is only a secondary one in the NO reduction, possibly leading to the formation of N<sub>2</sub>O by-product. A reaction mechanism operating in the reduction of NO with ammonia that involves the preliminary oxidation of NO to NO<sub>2</sub> or nitrite adspecies which then react with chemisorbed ammonia has been suggested by the authors for CuO/Al<sub>2</sub>O<sub>3</sub>. However a mechanism that involves the splitting of

ammonia coordinated on  $\text{Cu}^{2+}$  sites (to originate  $\text{Cu-NH}_2$ ) and the subsequent reaction of  $\text{Cu-NH}_2$  with NO (gaseous or weakly adsorbed) to form  $\text{N}_2$  and  $\text{H}_2\text{O}$ , has also been considered.

## 8. Catalysts activity in other catalyzed reactions of NO

It has been shown that all oxide catalysts that are active for SCR (reaction (3)) are also active for the oxidation of ammonia by dioxygen (reactions (7)–(9)), even if this is generally observed at higher temperatures. This means that all SCR catalysts are certainly able to activate ammonia.

However, it appears [150,152] that not all SCR catalysts are actually able to catalyze efficiently other reactions involving NO, such as its decomposition (the reverse of reaction (1)), its oxidation to  $\text{NO}_2$  (reaction (2)) and the reductions with reagents other than ammonia, such as CO,  $\text{CH}_4$  and  $\text{H}_2$ . Actually, Cu-based catalysts [21], e.g. Cu-ZSM5 zeolites but also bulk copper oxides or CuO supported on oxides [150,152], are reported to be very active in the decomposition of NO [177–179] and in the reduction of NO by light hydrocarbons [180,181]. Moreover, they are also active in the oxidation of NO to  $\text{NO}_2$  [182]. Bulk and supported CuO is also reported to be active in the reduction of NO by CO [150,152] and by hydrogen [183]. Metal-exchanged zeolites including Mn-ZSM5 and Fe-ZSM5 [184] are active in the reduction of NO by hydrocarbons in the presence of oxygen. On the other hand, also Fe, Cr and Mn are mentioned among the active catalysts for the NO reduction by CO,  $\text{CH}_4$  and  $\text{H}_2$  [150,152,185]. On the contrary, vanadia-based systems do not appear to catalyze efficiently these reactions [150,152,177].  $\text{V}_2\text{O}_5$ , as well as  $\text{WO}_3$  and  $\text{MoO}_3$ , has also been found almost inactive in NO decomposition [177].

From these data, and in agreement with the adsorption data reported above, it seems reasonable to conclude that while all SCR catalysts can act as activators for ammonia, they do not necessarily are able to activate NO. This supports the idea that NO reacts from the gas-phase, and in particular on  $\text{V}_2\text{O}_5$ -based catalysts that, apparently, are nearly unable to adsorb and hence to activate NO. As a matter of fact, isotopic labeling experiments showed that scrambling of the

NO oxygen atom with the catalyst V=O oxygen is possible to a limited extent [71,73], showing that NO is hardly able to interact with the catalyst surface. Furthermore, it has been shown [150,152,177] that NO decomposition is strongly inhibited by one of its own products, oxygen, due to its competition with the reactant NO on the active site. This agrees with the idea that NO does not adsorb over oxidized catalyst centers. This datum suggests that under actual SCR conditions, where oxygen is present in large excess together, NO cannot adsorb on oxide catalysts.

## 9. Proposed intermediate species, reaction schemes and reaction mechanisms for the SCR of $\text{NO}_x$ by $\text{NH}_3$

The mechanism of the SCR reaction and the nature of the species potentially active in it have been investigated over vanadia-based catalysts by several authors since the 1970s. Studies have been based on the results of reaction kinetics and of spectroscopic investigations of the adsorption of the reactants, that have been summarized in Sections 6 and 7, respectively. Similar studies have also performed on catalysts different from those based on vanadia.

The surface species that are supposed to be involved in the most popular reaction schemes among those proposed in the literature for SCR are summarized in Table 1 for vanadia-based catalysts and in Table 2 for other transition metal-based catalysts. However, prior to discuss them critically, some considerations must be done.

### 9.1. Introductory considerations

In the opinion of the present authors, a mechanism for an heterogeneously catalyzed reaction can be taken as “proposable” only if some requirements are fulfilled. These requirements are:

1. it allows to close a catalytic cycle with the correct stoichiometry;
2. it agrees with the known basic chemistry of reactants, products and, in case, of the supposed intermediate species;
3. it takes into account chemical species whose nature, bonds and charge, are fully clarified and reasonable, although tentative in case.

Table 1

Proposed reactant species, intermediates and active sites in different mechanisms and/or kinetic schemes for SCR on vanadia-based catalysts

Reactant species		Intermediate	Catalyst	Supposed active site	Reference
From NH <sub>3</sub>	From NO				
NH <sub>4</sub> <sup>+</sup>	O-N-O 		V <sub>2</sub> O <sub>5</sub>		Takagi et al. [67]
NH <sub>4</sub> <sup>+</sup>	NO gas	H-bonded complex	V <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} \text{O} \quad \text{OH} \\    \quad   \\ \text{-O-V-O-V-O} \end{array}$	Inomata et al. [68](a)
O-NH <sub>2</sub>   V	NO gas		V <sub>2</sub> O <sub>5</sub> /supp	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{-O-V-O-V-O} \end{array}$	Janssen et al. [71]
NH <sub>4</sub> <sup>+</sup>	NO gas		V <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} \text{OH} \\   \\ \text{V} + \text{V-O-V} \end{array}$	Gasior et al. [186]
NH <sub>2</sub>   V	NO gas	NH <sub>2</sub> NO   V	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	$\begin{array}{c} \text{O} \\    \\ \text{V} \end{array}$	Ramis et al. [123]
NH <sub>3</sub> ads NH <sub>2</sub>	N <sub>2</sub> Oads adsorbed NO		V <sub>2</sub> O <sub>5</sub> /supp V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	Lewis sites	Maragonzis et al. [105] Went et al. [50]
O <sup>-</sup> H <sub>3</sub> N <sup>+</sup> HO                V            V	NO gas	O <sup>-</sup> H <sub>3</sub> N-N=O HO                V            V	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	$\begin{array}{c} \text{O} \quad \text{HO} \\    \quad   \\ \text{-V-} \quad \text{-V-} \end{array}$	Topsøe et al. 1993 [173]
NH <sub>4</sub> <sup>+</sup>	O-NO <sub>2</sub>   V <sup>4+</sup>	NH <sub>4</sub> NO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	$\begin{array}{c} \text{O} \\    \\ \text{V}^{3+} \end{array}$	Kantcheva et al. [158]
NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>		V <sub>2</sub> O <sub>5</sub> /ZrO <sub>2</sub>		Indovina et al. [93]

Obviously, if the proposed surface intermediates have been observed spectroscopically, the proposal is strongly reinforced. Unfortunately, as discussed below, in our opinions not all the proposed mechanisms fulfill these requirements.

## 9.2. Some proposed mechanisms and intermediates

### 9.2.1. V<sub>2</sub>O<sub>5</sub>-based catalysts

One of the first reaction schemes for the SCR reaction over V<sub>2</sub>O<sub>5</sub>-based catalysts was proposed by Takagi et al. [67] 20 years ago. These authors proposed the formation of two different sites, denoted as l-O<sup>-</sup> (which is the product of dissociation of a surface hydroxy group l-OH) and l-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).

In Fig. 8 the very popular reaction scheme of Inomata et al. [68] is reproduced. It consists in the reaction of ammonium ion species with gaseous NO, throughout an “activated complex”. The electronic structure of this intermediate and the interactions occurring have not been specified. Moreover, the movements of electrons upon the reactions have not been hypothesized, and no sufficient chemical details are given. Nearly the same mechanism, without any detail for the movements of electrons, has been proposed by Gasior et al. [186] and Odenbrand et al. [107].

In Fig. 9 the mechanism proposed by Janssen et al. [71] is reproduced. In this case, adsorption of ammonia over a polyvanadate species O=V-O-V=O leads to

Table 2

Proposed reactant species, intermediates and active sites in different mechanisms and/or kinetic schemes for SCR on vanadia-based catalysts

Reactant species		Intermediate	Catalyst	Supposed active site	Reference
From NH <sub>3</sub>	From NO				
NH <sub>2</sub> ads	NO ads	an intermediate	Pd,CuOx		Otto et al. [159,188]
Cu <sup>2+</sup> (NH <sub>3</sub> ) <sub>n</sub> NO			Cu-Y		Mizumoto et al. [189]
NH <sub>2</sub>	NO		Fe <sub>2</sub> O <sub>3</sub>		Willey et al. [18](a)
S	S		Fe <sub>2</sub> O <sub>3</sub> -Cr <sub>2</sub> O <sub>3</sub>		Willey et al. [18](b)
ON NH <sub>2</sub>					
\ /					
M <sup>2+</sup>					
NH <sub>2</sub>	NO <sub>2</sub>		MnO <sub>x</sub> -WO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>		Kapteijn et al. [26]
□	*				
Cu(NH <sub>3</sub> ) <sub>n</sub> NO <sub>2</sub>			Cu-ZSM5	Dimers Cu <sup>2+</sup> (NH <sub>3</sub> ) <sub>n</sub>	Komarsu et al. [29]
HO NH <sub>2</sub>		NH <sub>2</sub> NO			
\ /	NO gas		MnO <sub>x</sub> -Al <sub>2</sub> O <sub>3</sub>		Kapteijn et al. [27]
Mn <sup>2+</sup>		HO-Mn <sup>2+</sup>			
NO <sub>2</sub> <sup>-</sup> NH <sub>3</sub>			MnO <sub>x</sub> -Al <sub>2</sub> O <sub>3</sub>		Kapteijn et al. [27]
\ /					
Mn <sup>3+</sup>					
NH <sub>2</sub> ads	NO ads		Cr <sub>2</sub> O <sub>3</sub>		Duffy et al. [24]
ON NH <sub>2</sub>		NH <sub>2</sub> NO			
\ /			CuO-Al <sub>2</sub> O <sub>3</sub>		Centi et al. [164]
Cu		Cu			
NO <sub>2</sub> <sup>-</sup> NH <sub>4</sub> <sup>+</sup>			CuO-Al <sub>2</sub> O <sub>3</sub>		Centi et al. [164]
\ /					
Cu-O					
NH <sub>2</sub>	NO gas	NH <sub>2</sub> NO			
			CuO/TiO <sub>2</sub>		Ramis et al. [19]
Cu		Cu			
NH <sub>3</sub>	NO <sup>+</sup>		Ce-mordenite		Ito et al. [168]
NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>		Ce-mordenite		Ito et al. [168]

the intermediate species V–ONH<sub>2</sub> (species D of Fig. 9) that is proposed as the key intermediate in the SCR reaction. Later, several authors [73,77,90,170] proposed the same intermediate species D as a key intermediate of SCR and/or ammonia oxidation on vanadia-based catalysts. However, none of them discussed the nature of this species on chemical grounds. This species is formally a dissociated form of hydroxylamine (NH<sub>2</sub>OH) which actually is a very weak acid (pK<sub>a</sub> 13.7) [171]. Metal complexes of hydroxylamine (through a coordination of the N atom

lone pair to the metal) are known [171] and can also be formed by hydroxylamine adsorption on metal oxide surfaces [134,169]. Transition metal complexes of the NH<sub>2</sub>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<sub>2</sub>O or nitrates, but N<sub>2</sub> can also be obtained, depending on the cation and on its concentration [171]. The reaction of Co-hydroxylamine complexes with nitrous acid has been shown to occur, but the product is N<sub>2</sub>O [187].

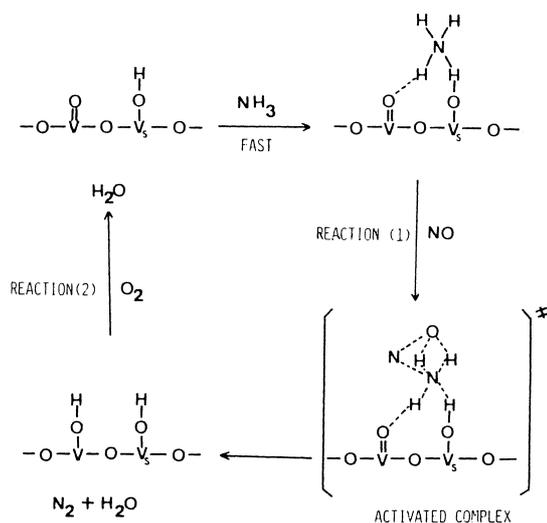


Fig. 8. Mechanism of the NO–NH<sub>3</sub> reaction on vanadium oxide catalysts proposed by Inomata et al. [68] in the presence of oxygen. Reprinted with permission from [68](c).

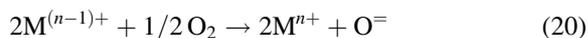
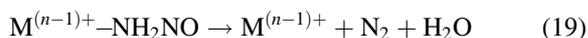
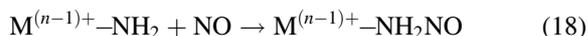
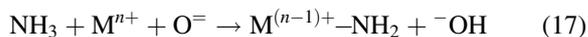
On the other hand, the formation of hydroxylamine (even in its dissociated form), from ammonia by oxidation with oxygen or transition metal cations, is quite unlikely. In fact, hydroxylamine was supposed to be an intermediate in ammonia oxidation to NO on platinum catalysts by Bodenstein [188], but this hypothesis seems to be now ruled out, in particular on transition metal oxides [81]. Hydroxylamine can actually be produced from ammonia by oxidation with hydrogen peroxide over Ti silicalite [189]. In any case, as reviewed recently by Matyshak and Krylov [190,191] no spectroscopic studies detected hydroxylamine-type species among the ammonia adsorption and oxidation products on any solid surface. More recent IR studies of hydroxylamine reaction over SCR catalysts further tend to exclude a role of such species in the reaction [134,169].

Ozkan et al. [73] proposed a similar species to act as a precursor for NH<sub>3</sub> oxidation to NO (Fig. 10, steps 1+2). They also proposed another species to be formed from ammonia on vanadia-based catalysts (depicted as V–ONH<sub>3</sub>) and produced by the reaction of V=O+NH<sub>3</sub>. This species is supposed to be a precursor for N<sub>2</sub> and N<sub>2</sub>O formation from ammonia (steps 3+4 and 3+5 of Fig. 10, respectively) or of N<sub>2</sub>O from NH<sub>3</sub>+NO (steps 3+6). The same inter-

mediate is used by Efstathiou and Verikios [170] in the scheme used as a base for their mathematical analysis of transient experiments of ammonia oxidation on V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub>. However, the chemical nature of these species is not discussed and is difficult to be interpreted.

The reactive NH<sub>3</sub> species involved in the SCR reaction has been depicted by Ozkan et al. [73] as V–ONH<sub>4</sub>. This species originates from NH<sub>3</sub>+V–OH (step 7 of Fig. 10) 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, but in this respect Ozkan et al. [73,90] use notations that do not allow to distinguish reduced from oxidized centers; also they do not try to close the catalytic cycles within their reaction schemes. Along similar lines, Efstathiou and Verikios [170] close a catalytic cycle for ammonia oxidation only taking into account the mass or atomic balances, but totally neglecting the electronic and charge balances. Accordingly, the corresponding conclusions are very difficult to be judged on chemical grounds.

In 1990 Ramis et al. [123] proposed the reaction pathway shown in Fig. 11, later proposed also for Cu-based catalysts [19]. This mechanism consists of the following steps:



Accordingly, ammonia is adsorbed over a Lewis acid site that activates ammonia to an amide NH<sub>2</sub> species (step 17), resulting in catalyst reduction. This activated ammonia species then react with gas-phase NO giving rise to a nitrosamide intermediate (step 18), that then decomposes to nitrogen and water (step 19). The reduced catalyst sites are then regenerated by gas-phase oxygen (step 20). The proper sum of these equations gives the reaction stoichiometry (3). The key reaction step is supposed to involve a radical coupling between the [M<sup>(n-1)+</sup>–NH<sub>2</sub>] surface species (whose amide moiety would act as a neutral radical),

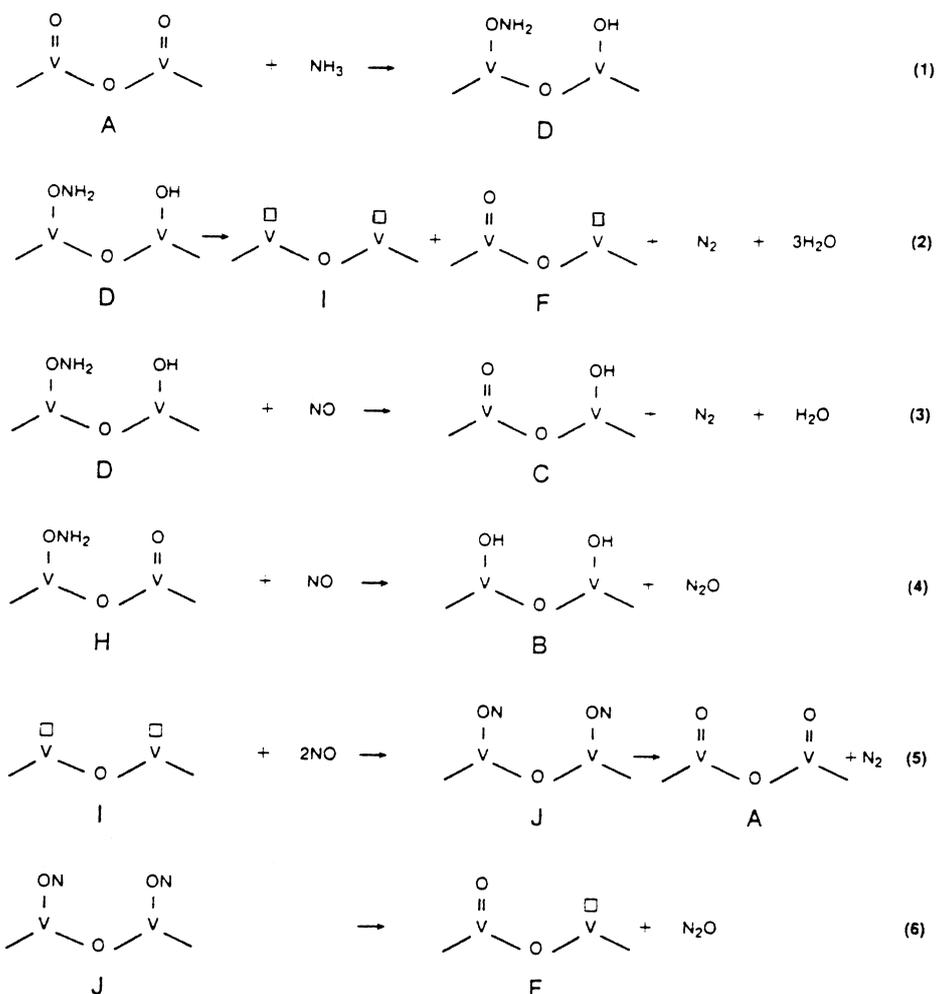
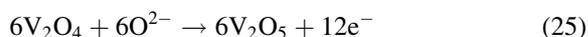
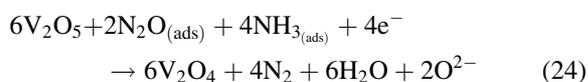


Fig. 9. Mechanism of the NO–NH<sub>3</sub> reaction on supported vanadium oxide catalysts proposed by Janssen et al. [71](b) in the presence of oxygen. Reprinted with permission from [71](b).

with the radical molecule NO. This is the first mechanism proposed for vanadia-based catalyst implying an activation of ammonia on Lewis acid sites. However, it is closely related to that first proposed by Otto et al. [192] for metal and CuO<sub>x</sub> catalysts and to the detection by Farber and Harris [175] of nitrosamide as a product of SCR. This mechanism will be referred as the “amide–nitrosamide” mechanism.

Few years later Went et al. [50] also proposed a mechanism implying the activation of ammonia in the form of an amide species. Although less details were given on the reaction step, it forecasts also ways for N<sub>2</sub>O formation.

Marangozis [105], in a kinetic study of the DeNO<sub>x</sub>-SCR reaction over vanadium oxide catalysts, proposed a reaction mechanism based on the following steps:



Steps (22) and (23) correspond to the chemisorption of NO and O<sub>2</sub>, respectively; step (24) is the reaction of

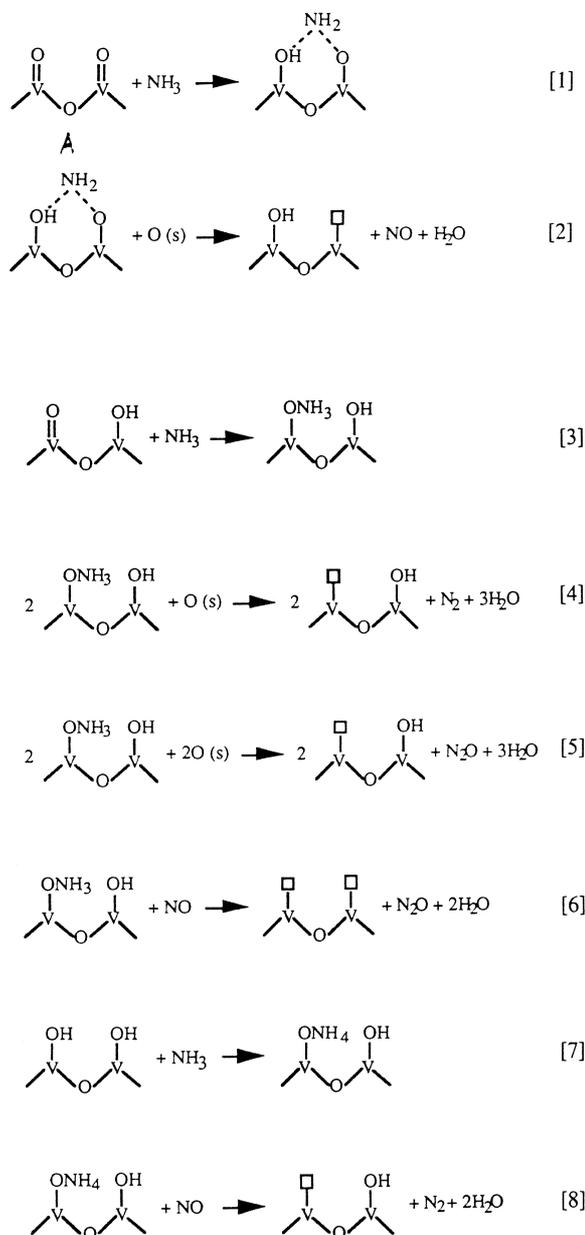


Fig. 10. Mechanism of the NO–NH<sub>3</sub> reaction on vanadium oxide catalysts proposed by Ozkan et al. [73](b) in the presence of oxygen.

N<sub>2</sub>O<sub>(ads)</sub> with NH<sub>3(ads)</sub> whereas step (25) is the catalyst reoxidation. This mechanism, however, is not based on experimental evidences and, as discussed below, is not consistent with the agreed mechanistic features of the reaction.

Quite recently, on the basis of in situ on-line FTIR studies under steady-state conditions, Topsøe et al. [173] proposed the mechanistic scheme shown in Fig. 12. In this mechanism, the catalytic activity is found to be related to the ammonia adsorbed on the Brønsted acid sites associated with V<sup>5+</sup>–OH sites. V<sup>5+</sup>=O 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 a hydrogen from the NH<sub>3</sub> molecule and accordingly reduced V<sup>4+</sup>–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<sup>4+</sup>–OH sites to V<sup>5+</sup>=O groups) occurs by gas-phase oxygen. Accordingly, the proposed catalytic cycle consists of both acid–base and redox functions. It is noted that this mechanism can be seen as a modification of the mechanism of Ramis et al. [123], in which the ammonia adsorption sites are considered to be Brønsted acid sites instead of Lewis acid sites. These authors much emphasized their proposed mechanism that also supposes a kinetic role for a species depicted as NH<sub>3</sub><sup>+</sup>, which would be a radical-cation produced by extracting an electron from ammonia. The possibility of this species to be proposed as an intermediate involved in a slow step (as they in fact suppose) and to react as such with NO is very unlikely on chemical grounds in the opinion of the present authors, and should be supported by more convincing data. Additionally, Topsøe et al. [173] were not able to follow the behavior of coordinated NH<sub>3</sub> because the spectral region below 1300 cm<sup>-1</sup> was cut in their spectra. This point will be further discussed below.

### 9.2.2. Other oxide catalysts

In one of the earliest studies of the SCR reaction on metal based catalysts (but including also possibly oxidized Cu) Otto and Shelef [192] proposed the reaction occurring between an –NH<sub>2</sub> amide species and NO, through an “intermediate”. A similar mechanism was also used by Willey et al. [18] in their kinetic study of the SCR over Fe<sub>2</sub>O<sub>3</sub>-based catalysts. Later, Mizumoto et al. [193] proposed that on Cu-exchanged zeolites a reaction involving a nitrosyl-amino Cu(II) complex (Cu<sup>2+</sup>(NH<sub>3</sub>)<sub>n</sub>NO).

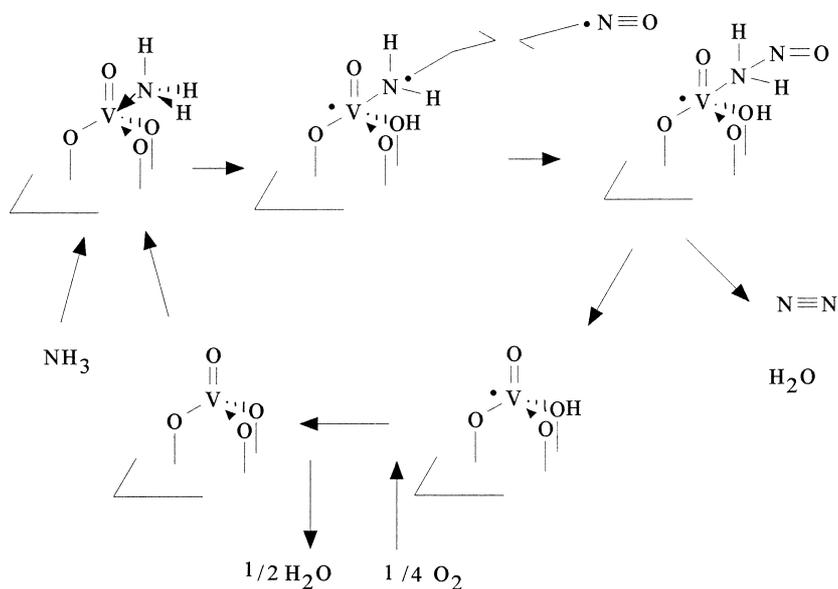


Fig. 11. Mechanism of the NO-NH<sub>3</sub> reaction on supported vanadium oxide catalysts proposed by Ramis et al. [123] in the presence of oxygen.

### DeNO<sub>x</sub> Catalytic Cycle

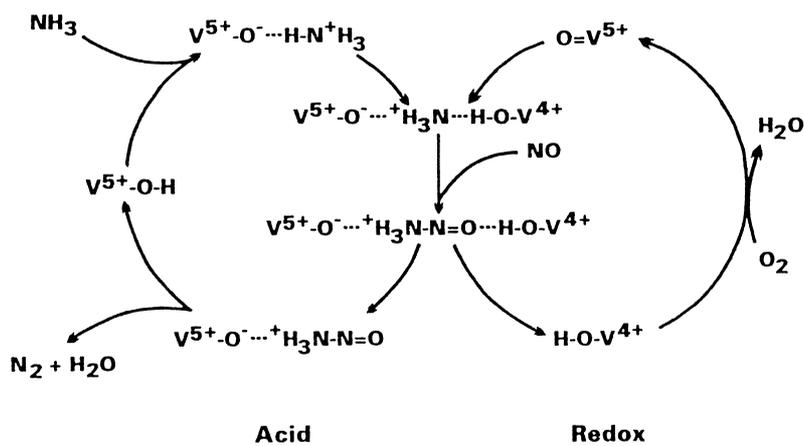


Fig. 12. Scheme illustrating the catalytic cycle of the SCR reaction over vanadia/titania catalyst in the presence of oxygen proposed by Topsøe et al. [173]. Reprinted with permission from [173](c).

A more complex mechanism has been proposed by Komatsu et al. [29] for Cu-zeolite catalysts (Fig. 13). In this mechanism, a molecule of NO and a dissociated oxygen atom react with the oxygen atom of a suggested active NH<sub>3</sub>-Cu dimer species (species (a) of Fig. 13), thus resulting in the formation of a bridging

NO<sub>3</sub> species. To explain the observed first order rate in NO and half order in O<sub>2</sub>, the step from (a) to (b) has been considered as the rate-determining step. Then another NO molecule attacks the NO<sub>3</sub> species to form two NO<sub>2</sub> molecules, each attacked to a Cu atom (species (c)). Finally, the reactive NO<sub>2</sub> species and

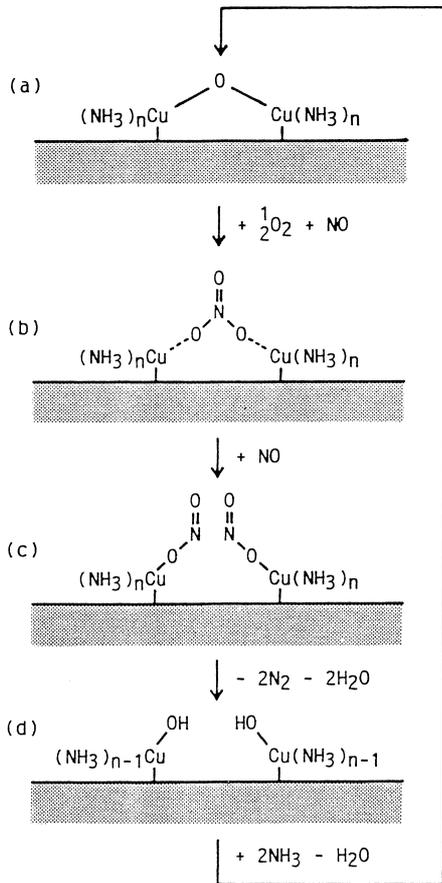
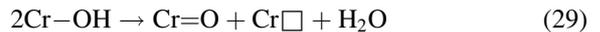
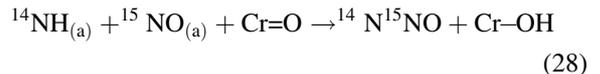


Fig. 13. Scheme illustrating the catalytic cycle of the SCR reaction over Cu-ZSM5 catalyst in the presence of oxygen proposed by Komatsu et al. [29]. Reprinted with permission from [29].

one of the  $\text{NH}_3$  ligands bound to the same Cu ion react to produce nitrogen and water. Although these authors do not count explicitly the electrons, the proposed reaction intermediate is necessarily a nitrite species  $\text{NO}_2^-$ , formed by reaction of a nitrate species,  $\text{NO}_3^-$ , with NO and Cu. However this complex chemistry should be supported by more data.

Centi et al. [21,164] proposed for Cu/ $\text{Al}_2\text{O}_3$  the reaction scheme reproduced in Fig. 14, where the SCR reaction can occur either via formation of an amide  $\text{NH}_2$  species that then reacts with NO to form a nitrosamide intermediate (as suggested in the case of  $\text{V}_2\text{O}_5/\text{TiO}_2$  [123]), or via oxidation of NO to  $\text{NO}_2$  or nitrite species which then react with chemisorbed ammonia. Formation of  $(\text{NO}_3)^-$  species is also possible, leading to the formation of ammonium nitrate species that are responsible for the formation of  $\text{N}_2\text{O}$ .

On the basis of isotopic labeling studies, Duffy et al. [24] proposed the following model for  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation over amorphous and crystalline chromia:



where NH species are produced by  $\text{NH}_2$  dissociation. This mechanism is, however, only tentative since it is

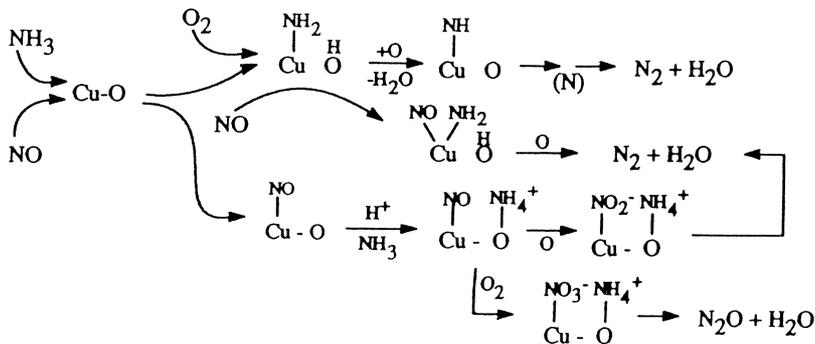


Fig. 14. Scheme illustrating the mechanism of the NO- $\text{NH}_3$  reaction over Cu-based catalyst in the presence of oxygen proposed by Centi et al. [21]. Reprinted with permission from [21].

not supported by any data concerning the nature of the reactive surface intermediates.

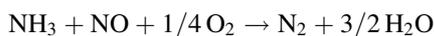
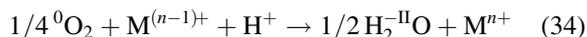
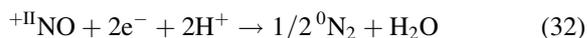
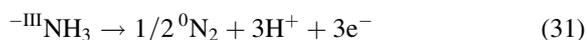
Finally, a comment can be deserved to the kinetic scheme proposed by Kapteijn et al. [26] and Singoredjo [96] for Mn-based catalysts. These authors define their kinetic model as a two-site mechanism with (oxidative) adsorption of NO in the form of NO<sub>2</sub>. However, an analysis of their scheme easily indicates that the mechanism actually implies three sites and NO conversion to an “NO<sub>2</sub>” species whose charge is not defined. This species actually reacts as NO, so that no NO oxidation occurs. This kinetic work is an excellent one but the proposed mechanism where the number of electrons and charges is neglected is an example of incorrect use of chemical symbols giving rise to incorrect conclusions.

### 9.3. Stoichiometry constraints to the reaction mechanism

Many different ways and reaction schemes are possible, in theory, to perform the reduction of NO<sub>x</sub> by ammonia. However, the possible mechanisms are limited by the hypotheses accepted today by almost all authors. They are:

1. the reaction stoichiometry is Eq. (3);
2. the reaction is actually a coupling reaction, i.e. one N atom of the N<sub>2</sub> product comes from NO and the other from NH<sub>3</sub>;
3. N<sub>2</sub>O is not an intermediate;
4. the mechanism is of the redox type, i.e. O<sub>2</sub> oxidizes the surface sites reduced by other reactants.

Under these generally accepted hypotheses, the reaction scheme proposed by Marangozis [105], that contradicts points 2 and 3, is ruled out. Also, the possible reaction mechanisms restrict very much. Reaction (3) is indeed a redox reaction where one reductant (ammonia, nitrogen oxidation state –III) and two oxidants (NO, nitrogen oxidation state +II, and dioxygen, oxygen oxidation state 0) react, giving rise to dinitrogen (nitrogen oxidation state 0) and water (oxygen oxidation state –II). This redox reaction can be decomposed in semi-reactions in the usual way. By adding also the redox catalyst cycle, the following steps can be proposed:



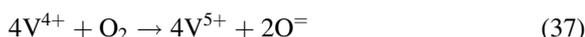
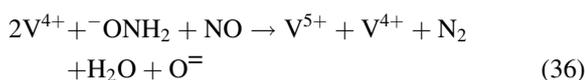
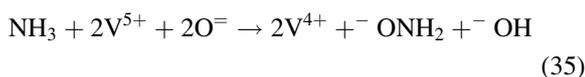
It is evident that the simplest way to accomplish this reaction implies the reduction of both oxidants (NO and oxygen, or, better, NO and the oxidized catalyst site) by the reductant (ammonia). In this case, a very simple possibility concerning the sequence of the two steps is that ammonia takes one electron from the oxidized surface site first (giving rise to an activated species with oxidation state –II), and two electrons from NO later. This scheme corresponds to both the “nitrosamide-type” mechanism discussed above (ammonia activated species neutral amide NH<sub>2</sub>) and to the mechanism of Topsøe et al. [173] (ammonia activated species NH<sub>3</sub><sup>+</sup> ion).

Another possible reaction scheme implies first the oxidation of the oxidant NO by the other oxidant (O<sub>2</sub> or the oxidized catalyst site) to an intermediate species; this species must have nitrogen oxidation state +III (like nitrite ions, NO<sub>2</sub><sup>-</sup>, or NO<sup>+</sup>) and would later oxidize ammonia to 1/2 N<sub>2</sub>, providing itself the other 1/2 N<sub>2</sub>. In view of the weak adsorption of NO on the vanadia-based catalysts, the mechanisms that imply NO oxidation seem to be excluded on these kinds of catalysts. On the other hand, such chemistry has been proposed by Komatsu [29] (Fig. 13) and by Centi [21,164] (Fig. 14) over Cu-based catalysts, where NO adsorption is significant.

It is worth noting that the oxidation of ammonia to 1/2 N<sub>2</sub> provides no more than three electrons. So ammonia can reduce to 1/2 N<sub>2</sub> (the other half nitrogen molecule) the N-containing species (arising from NO) only if it has oxidation state not higher than +III. This means that NO<sub>2</sub> (N oxidation state +IV) and nitrates (N oxidation state +V), both of which have been suggested as possible active species [27,67,93,96, 111], cannot be the actual reactant. Nitrogen oxide species with N oxidation state higher than +III, if produced by NO oxidation, must decompose back to a species with oxidation state not higher than +III before reacting with ammonia. Thus, they only can have a role of storage of NO, if any. In any case, the way involving previous NO oxidation implies strong adsorption of NO on the catalyst, what seems excluded

on vanadia-based catalysts. On the other hand, it is noted that  $\text{NO}_3^-$  (or  $\text{NO}_2$ ) can have a role in the formation of  $\text{N}_2\text{O}$  by-product, as suggested by Centi [164] over Cu-based catalysts.

The scheme proposed by Janssen et al. [71] (Fig. 9) is more complex from the point of view of the redox behavior. This mechanism implies the activation of ammonia to oxidation state  $-I$  (adsorbed hydroxylamine, see above). These authors do not show explicitly the oxidation state of the V centers, but their reaction scheme certainly corresponds to the following steps:



It is observed that upon the reaction, only one of the two electrons to reduce NO is taken from the nitrogen atom arising from ammonia, while the other is taken from one of the two vanadium centers. This means that, of the two vanadium sites, one is reduced by ammonia and reoxidized by oxygen, the other is reduced by ammonia and reoxidized by NO. This way, although in our opinion is unlikely in relation to the known chemistry of hydroxylamine, is possible in principle.

Other possibilities are conceivable from the stoichiometry point of view. Some of them imply complex redox cycles (with species oxidized and reduced more than one time), others involve reduction of NO by the reduced catalyst sites. However, all of them are apparently to be ruled out on the basis of adsorption data, at least over vanadia-based catalysts.

## 10. On the active sites and mechanism of the $\text{NO}_x$ SCR by $\text{NH}_3$ on vanadia-based catalysts

### 10.1. Nature of the active sites

There is now a general agreement on the fact that the active sites are or contain the vanadium ions. Also, as already discussed in Sections 6 and 7, almost all

authors (with few exceptions [93]) agree that on vanadia-based catalysts ammonia reacts from a strongly adsorbed state while NO adsorption is more or less negligible. However, the debate is still open concerning the nature of the active sites and of the active ammonia species. According to the adsorption data discussed above, ammonia activation could, alternatively, occur on Lewis sites (active species: coordinated ammonia and/or amide species) or on Brønsted sites (active species ammonium ions or  $\text{NH}_3^+$  cations). A key role of Brønsted acidity has been supported by several authors, on the basis of the following reasons:

1. ammonium ions were the only observed species from ammonia adsorption on  $\text{V}_2\text{O}_5$  [67,68,187];
2. water was reported to accelerate the reaction [66];
3. very strong Brønsted acidic materials like sulfated titania [41] and zeolite H-ZSM5 [29] show SCR activity;
4. additives increasing the Brønsted acidity, like  $\text{WO}_3$  [64] and sulfates (see [12,43](b)) for  $\text{V}_2\text{O}_5\text{-TiO}_2$  and sulfates for  $\text{TiO}_2$  [41,131], also increase catalytic activity;
5. IR studies showed that ammonium ion species are very evident on vanadia-based catalysts, and (a) according to Topsøe et al. [173], they would decrease their amount upon reaction with NO; (b) Schneider et al. [127] reported that the SCR activity correlates with the fraction of Brønsted-bound ammonia.

On the other hand, all the above data are contradicted or corrected by other data, and in particular:

1. Ramis et al. [123], in agreement with previous data of Belokopytov et al. [119], showed that surface vanadium centers of vanadia, both bulk and supported, also display Lewis acidity. On the other hand, all authors agree on the presence of Lewis acidity, together with Brønsted acidity, on supported vanadia catalysts.
2. Most authors agree today that water inhibits the SCR reaction [100–109], likely due to a competition with ammonia on the Lewis sites.
3. The activity of materials like sulfated titania and H-ZSM5 zeolites occurs at very high temperatures and may involve transition metal impurities [29].
4. Sulfation and addition of tungsten oxide increases also Lewis acidity of  $\text{V}_2\text{O}_5\text{-TiO}_2$  [15,36] and also perturb their redox states [33,37]. Moreover,

according to Deo and Wachs [49](c), they can simply offer a second reaction site, possibly a site for weak NO adsorption [189].

5. The IR data of Topsøe et al. [173] contradict by those of Ramis et al. [123,126,132] that clearly show the reaction of Lewis bonded ammonia with NO. On the other hand, the data of Topsøe et al. [173] are not obtained in the best conditions to follow the behavior of coordinated ammonia because the spectral region below  $1300\text{ cm}^{-1}$  was cut in their spectra.

Conversely, it has been shown that catalysts where Brønsted acidity is absent or very weak, such as CuO–TiO<sub>2</sub> [19], MnO<sub>x</sub>–TiO<sub>2</sub> [146], Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> [146], Fe<sub>2</sub>O<sub>3</sub> [18,19,145], and also pure TiO<sub>2</sub> [131] are also more or less active SCR catalysts. The curves in Figs. 2 and 3 show that catalysts with strong or no Brønsted acidity exhibit a parallel behavior. This shows that Brønsted acidity is per se not necessary for SCR activity, at least at low temperatures.

On the other hand, coordination of ammonia on a reducible cation is a very reasonable first step towards ammonia partial oxidation, which necessarily should occur upon SCR and consists in the migration of electrons from ammonia to the catalyst site. Instead, the protonation of ammonia is not a step towards oxidation, since to be oxidized and to perform the SCR process, ammonia must lose electrons and protons. To give it a proton more is useless.

In addition to the nature of the reactive sites (i.e. Lewis and/or Brønsted acid sites), another relevant question is whether the SCR reaction can occur on a single site or needs two adjacent sites, as proposed by Wachs et al. (see [49](c) and [174]). These authors observed that in the case of sub-monolayer V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> catalysts the V turn-over frequency in the SCR increases by either increasing the vanadium coverage or by addition of tungsten oxide. This was interpreted as due to the need of a couple of near-by sites for the reaction, and specifically of a surface V redox site and of an adjacent non-reducible metal oxide site. In this respect, we note that also the mechanism proposed by Topsøe et al. [173] involves a catalyst redox and a distinct acid function.

The effect of the vanadia loading and of the addition of WO<sub>3</sub> on the reactivity of TiO<sub>2</sub>-supported vanadia catalysts in the SCR reaction has also been investigated by Lietti et al. [36,37,53,137,138,176]. In line

with other studies, it has been found that the catalysts reactivity is significantly increased by either increasing the V<sub>2</sub>O<sub>5</sub> or the WO<sub>3</sub> loadings. When the V loading is increased, the higher reactivity of the catalysts can be related to the formation of polymeric metavanadate species. The reactivity of such species, in line with previous results reported by Went et al. [50], is higher than that of isolated vanadyls, due to their superior redox properties [33,50]. In particular it has been suggested that the increase in the number of the surface V and/or W sites causes a perturbation of the electronic structure of the solid [33,37]. In fact, the d orbitals of isolated V centers lie into the gap of the semiconductor TiO<sub>2</sub> phase, while apparently those of W lie in the conduction band [37,194]. When the solid is slightly reduced, V centers trap the electrons and their d orbitals play the role of donor levels of the n-type semiconducting solid. By increasing V concentration, the conductivity of the n-type semiconductor increases. If polymeric vanadate species grow, more complex electronic structures are formed, with peculiar redox behavior. The addition of W also increases the reducibility (and the conductivity) of the solid [34,36,37]. So, by increasing the coverage of TiO<sub>2</sub> with V- and W-oxide centers, the redox properties of the V-centers can be improved, and their own activity increased, even if they work as single sites. The rate of catalyst reoxidation can be also strongly enhanced.

These interpretations contrast with the data reported by Wachs et al. [174] who observed that the catalyst redox properties, probed by the methanol oxidation reaction, do not depend on either the V or W loading. Along similar lines, recently Andreini et al. [195] showed that WO<sub>3</sub> increases the activity also of vanadia–alumina: alumina is an insulator and accordingly should not interact electronically with the V and W surface species.

It is worth to note that other catalyst components, although inactive or poorly active in the SCR (e.g. the W and/or Ti surface sites), may have a role in the reaction. The effect of WO<sub>3</sub> on the catalyst redox properties has been already discussed above. Also, W and/or Ti surface sites strongly adsorb ammonia [50,136,137] and accordingly they participate in the reaction as “reservoir” of adsorbed NH<sub>3</sub> species, as discussed in Section 7.4.1. These aspects may be relevant in the case of samples having composition similar to that of commercial catalysts, i.e. very low V

loading and high W and Ti surface coverage. Accordingly, a distinction should be made between the ammonia “adsorption” and “reaction” sites, and care must be taken when discussing, e.g. spectroscopic data of the SCR mechanism (indeed in this case the contribution of the bands arising from  $\text{NH}_3$  adsorbed on the  $\text{TiO}_2$  support are superimposed to those corresponding to the active sites) or in the derivation of kinetic models (the  $\text{NH}_3$  adsorption sites differ from the  $\text{NH}_3$  reaction sites) [144].

### 10.2. Reaction mechanisms

In the previous sections a number of proposed reaction mechanisms for the SCR reaction over  $\text{V}_2\text{O}_5$ -based catalysts have been briefly summarized. Some of the mechanistic information previously discussed have been obtained from catalytic activity data performed under conditions representative of the real SCR conditions (e.g. presence of water vapor,  $\text{SO}_2$ ), but the majority of the mechanistic data come from spectroscopic studies that have been performed under “clean” conditions and over “model” catalysts. Accordingly, care must be adopted in order to extrapolate these data to real working catalysts. In spite of these difficulties, several mechanistic features of the SCR reaction are well established and commonly accepted in the literature.

In particular, it is the opinion of the present authors that the overall set of data discussed above strongly support for the SCR reaction over  $\text{V}_2\text{O}_5$ -based catalysts the so-called “amide–nitrosamide” mechanism. The reasons supporting this mechanism are the following:

1. many data suggest that the reaction occurs on Lewis sites, on vanadia like on several other catalysts;
2. most authors agree that NO does not necessarily adsorb before reacting;
3. traces of amide species  $-\text{NH}_2$  have been actually found in the IR spectra of adsorbed ammonia on several SCR catalysts;
4. IR studies showed that coordinated ammonia species progressively disappear upon reaction with NO, and traces of amide species were no more found spectroscopically;
5. nitrosamide  $\text{NH}_2\text{NO}$  was detected by mass spectrometry among the reaction products of SCR on

vanadia-based catalysts [175] and traces of it were also found by IR spectroscopy at the catalyst surface [123];

6. kinetic data can be successfully interpreted on the basis of this mechanism;
7. no ascertained published data contradict this mechanism;
8. this mechanism involves species that have examples in organometallic and inorganic chemistry and appears to be fully reasonable from the chemical point of view;
9. this mechanism fulfills the conditions summarized in Section 9.3 and the additional one, arising from experimental data [71], that part of water arises directly from the reactants and part from a surface dehydration step;
10. this mechanism is, *mutatis mutandis*, what is also thought to occur in the gas-phase [196] in the so-called SNCR (selective non-catalytic reduction) where the intermediacy of the nitrosamide species has been proposed, as well as on metal catalysts [187];
11. this mechanism is not contradicted by the inhibiting and promoting effects of  $\text{H}_2\text{O}$  and sulfates on the SCR reaction, respectively, that are observed under real operating conditions.

### 11. On the active sites and mechanism on other transition metal-based catalysts

As it can be easily deduced from Table 2, better agreement exists among authors working on Fe-, Cu-, Cr- and Mn-based catalysts, than among those working on vanadia-based catalysts. Almost unanimously they think that reaction occurs on the transition-metal cationic center (Lewis sites), where both ammonia and NO could adsorb. However, in almost all cases an adsorption of both NO and ammonia is supposed to take place before reaction. This agrees with spectroscopic and thermal desorption measurements, that showed non-negligible adsorption of NO, as well as with the activity of these catalysts also on other catalytic reactions of NO. However, also in these cases, the mechanism via amide–nitrosamide has several supporters. However, mechanisms where oxidation of NO to  $\text{NO}_2^-$  cannot be excluded in some cases,

like on Cu-exchanged zeolites, in our opinion, because in this case strong adsorption of NO can occur.

## 12. A comparison of the SCR of NO by NH<sub>3</sub> with the SCR of NO by hydrocarbons on transition metal-exchanged zeolite catalysts

The data discussed above allow some comments in respect to the relations between the different NO reduction processes. In particular, it must be noted that in the case of the reaction of NO with hydrocarbons the reducing agent supplies much more electrons than ammonia (that only provides three electrons). For example, the oxidation of <sup>-IV</sup>CH<sub>4</sub> to <sup>+IV</sup>CO<sub>2</sub> + 2H<sub>2</sub>O provides eight electrons. Even more electrons are supplied by higher hydrocarbons. This means that, in this case, highly oxidized species arising from NO, like <sup>+IV</sup>NO<sub>2</sub> and <sup>+V</sup>NO<sub>3</sub><sup>-</sup>, can be reduced by the reductant to N<sub>2</sub>, and can consequently act as active species. On the other hand, NO must supply both N atoms of the resulting N<sub>2</sub> molecule, instead of only one, and this suggests that “symmetric” intermediates can occur, more than asymmetric intermediates like those forecasted when NH<sub>3</sub> is the reductant (like NH<sub>2</sub>-NO, nitrosamide).

Finally, it is evident that in the SCR process (reaction (3)) the reductant, i.e. ammonia is the most polar and most strongly adsorbed reactant, due to its basicity and to the acid character of most catalysts. When the reductant is a hydrocarbon, the reverse is true: indeed in this case the reducing agent is by far less polar and less strongly adsorbed than the oxidant. Consequently, in the first case the catalyst activates ammonia, and reaction occurs between the reductant in the adsorbed state and gaseous NO. In the latter cases, instead, the catalyst activates NO and the reaction occurs between adsorbed oxidized NO and the reductant in the gas-phase. These features make these two reactions very different, as obvious, and suggest that, although reactions (3) and other reductions with hydrocarbons have one reactant in common and some solids can catalyze both, their mechanisms have nothing in common.

## 13. Conclusions and future research

The analysis of the data reported in the scientific literature concerning the chemical details of the SCR

reaction on both vanadia-based catalysts (models and industrial catalysts) and on other transition metal oxide catalysts shows that the debate on the mechanistic and chemical aspects of the reaction is still open, but also indicates that quite a converging picture could be obtained. In the case of vanadia-based catalysts, in particular, almost all authors agree that the SCR reaction does involve a strongly adsorbed activated ammonia species and a gas-phase or weakly adsorbed NO species, according to an Eley–Rideal mechanism. A different picture may hold over other metal oxide catalysts, where oxidation of NO could also occur and accordingly the SCR reaction may also proceed via a Langmuir–Hinshelwood mechanism.

However, several details on the proposed reaction schemes are still to be better clarified. These aspects include the catalyst characterization, the nature of the active sites, the effects of additives and poisons, etc. In particular the following points deserve additional studies and investigations:

1. The characterization of the catalysts is still uncompleted. In the case of industrial V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>–MoO<sub>3</sub>–TiO<sub>2</sub> catalysts, the “monomeric” vanadyl, wolframyl and molybdenyl species have been well characterized by using vibrational spectroscopies and some other spectroscopic techniques such as <sup>51</sup>V NMR. However, the existence of “polymeric” species such as V<sub>x</sub>O<sub>y</sub> polyvanadates and mixed V–Mo and V–W oxide species can be suspected, and their role in the reaction, if actually existing, is still far from being completely clarified.
2. The question, whether the SCR mechanism needs two sites or if the reaction can occur on a single site, is still open. There is no doubt, in our opinion, that the reaction calls for a catalyst “redox” and “acid” function, but still is not clear whether this does actually mean that the reaction needs two separate although adjacent sites to occur.
3. Also, the role of other species present at the catalyst surface, e.g. W oxide species or SO<sub>4</sub><sup>-</sup> ions, deserves additional studies. It is known that WO<sub>3</sub> and sulfates increase the catalyst activity, but it is not clear so far whether these species exert their promoting effects by providing the second adjacent site to the active V-sites (if the reaction proceeds according to a dual-site mechanism), or by affecting the electronic properties of the catalyst (i.e. by modifying

the collective properties of the surface active sites), or via structural modification of the active V sites (e.g. via the formation of new species).

4. The exposed Ti surface may also have a role in the reaction. Indeed Ti-sites may act as NH<sub>3</sub> storage that can be provided to near-by active V-sites. Also, care must be taken when extracting mechanistic information from spectroscopic data where the contribution of the bands arising from NH<sub>3</sub> adsorbed on the TiO<sub>2</sub> support can be superimposed to those corresponding to NH<sub>3</sub> present onto the active sites.
5. A challenge for the future is to provide new experimental data more directly related to “real” catalyst working under “real” conditions. Indeed most of the reactivity and mechanistic studies reported in the literature refer to “model” catalysts and “clean” conditions, e.g. catalysts with compositions very far from those of commercial samples, absence of water vapor and SO<sub>x</sub> in the gas stream, vacuum conditions or reactant partial pressures very far from those corresponding to real industrial application. Accordingly, several questions arise concerning the extendibility of these results to commercial catalysts under actual working conditions, and care must be adopted when extrapolating mechanistic information from these studies.
6. The SCR reaction occurs in parallel with many other potentially competitive reactions. This makes the picture concerning activity and selectivity very complex, also because of the presence of water vapor, SO<sub>x</sub> and, possibly, As containing species, that likely influences differently the activity and the selectivity of the different catalysts in the main reaction and in the undesired side-reactions.
7. Another important question is related to the production of N<sub>2</sub>O by-product. The formation of this product must be avoided in relation to its greenhouse effect. The origin of this species has not been clarified so far, and accordingly additional studies are needed.
8. Finally, the role of NO<sub>2</sub> in the SCR chemistry has not been fully addressed so far, in our opinion. In spite of the fact that this species represents only a minor fraction of the total NO<sub>x</sub>, it can play a significant role in the reaction mechanism. This point is not completely clear and needs additional studies to be better understood.

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