ELSEVIER

Catalysis Today 45 (1998) 85–92

CATALYSIS TODAY

Transient kinetic study of the SCR-DeNO$_x$ reaction

Luca Lietti*, Isabella Nova, Enrico Tronconi, Pio Forzatti

Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, P.zza L. Da Vinci 32, 20133 Milano, Italy

Abstract

The unsteady-state kinetics of the selective catalytic reduction (SCR) of NO with NH_3 is studied over V_2O_5–WO_3/TiO_2 model catalysts by means of the transient response method. NH_3 strongly adsorbs onto the catalyst surface whereas NO does not adsorb appreciably. A dynamic mathematical model based on a Temkin-type desorption process for NH_3 and a SCR reaction rate with a complex dependence on the ammonia surface coverage is well suited to represent the data. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic reduction (SCR); Vanadia-based catalysts; Transient kinetic study; Ammonia adsorption-desorption; SCR, dynamic model

1. Introduction

The NO_x removal from the flue gases of stationary sources (DeNO$_x$ing) is efficiently achieved by using the SCR (selective catalytic reduction) technique. In this process, ammonia is injected in the flue gases and NO_x are eliminated via following reaction [1,2]:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \quad (1)$$

Operation of industrial SCR reactors often involves transient conditions associated e.g. with load variations and start-up or shut down of the plant. Also, the SCR technology has been proposed for NO_x abatement in systems characterized by fast load changes, such as diesel engines [3,4].

Accordingly, a study of the DeNO$_x$ reaction under non-stationary conditions has been undertaken in our labs, aiming at obtaining additional insight on the dynamics of the SCR process and on the mechanistic features of the reaction under both steady- and unsteady-state conditions. For this purpose, the transient response method [5] has been applied: perturbations are imposed to the reacting system (e.g. step changes in the inlet reactant concentration) and the transient response is analyzed. The characteristics of the response reflect the sequence of the elementary steps of the reaction, therefore, these methods are able to provide, in principle, mechanistic evidence that cannot be collected under steady-state conditions, where all the steps of the reaction are progressing at the same rate. Finally, in order to obtain quantitative kinetic indications, the results of the transient experiments have been analyzed according to a simple dynamic model of the reacting system.

2. Experimental

Sub-monolayer V_2O_5/TiO_2 (V_2O_5=1.47% w/w, θ_V=0.21, S_a=46 m^2/g) and V_2O_5–WO_3/TiO_2

*Corresponding author. Tel.: +39-02-23993272; fax: +39-02-70638173; e-mail: luca.lietti@polimi.it

0920-5861/98/$ – see front matter
PII: S0920-5861(98)00253-3

(V_2O_5=1.47% w/w and WO_3=9% w/w, θ_V=0.12, θ_W=0.67 and S_a=80 m^2/g) model catalysts were used in this study. The transient experiments were performed in a flow-microreactor system, consisting in a small quartz tube (6 mm i.d.) connected to a mass spectrometer. The reactor contained 160 mg of catalyst (60–100 mesh). A stream of He+1% v/v O_2 (120 cc/min STP) was used, containing 700 ppm NH_3 and 700 ppm NO. Abrupt switches in the reactant feed concentration were performed by means of a four-port valve positioned at the reactor inlet. Further details on the catalyst preparation and characterization and on the apparatus can be found elsewhere [6,7].

3. Results and discussion

3.1. Transient kinetics of NH_3 and NO adsorption–desorption

The dynamic adsorption–desorption of the SCR reactants (i.e. NH_3 and NO) in flowing He+1% v/v O_2 has been investigated at first. A typical result obtained in the case of a rectangular step feed of ammonia performed at 220°C over the V_2O_5–WO_3/TiO_2 model catalyst is presented in Fig. 1(A), along with the ideal ammonia inlet concentration (dashed lines). Upon the NH_3 step addition (at t=0 s), the ammonia reactor outlet concentration slowly

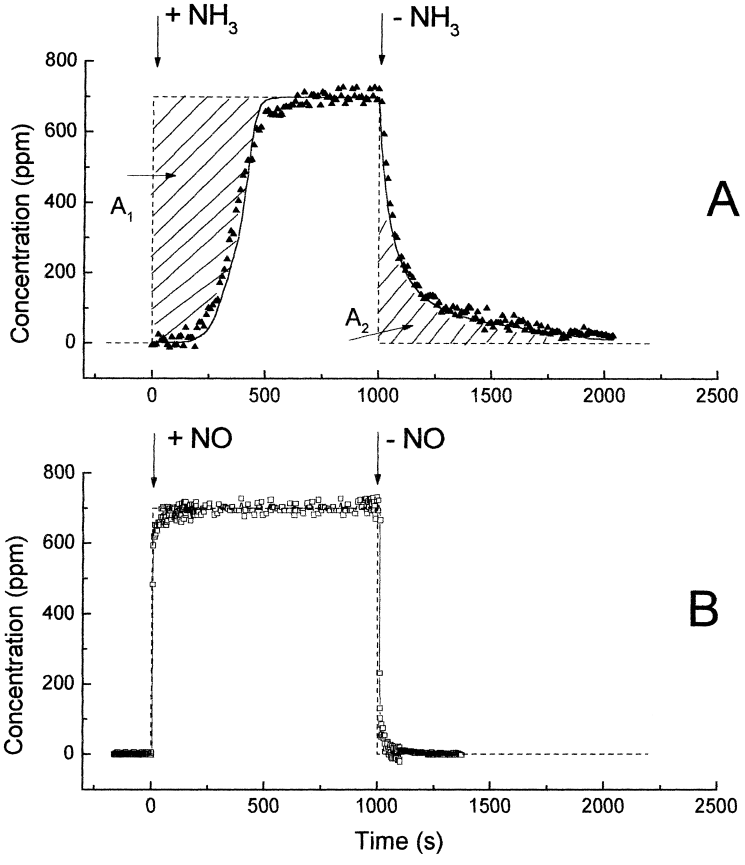

Fig. 1. Dynamic adsorption–desorption of NH_3 (A) and NO (B) on a model V_2O_5–WO_3/TiO_2 catalyst at 220°C. Dashed line: ideal step; solid lines: model fit.

increased with time, approaching the ammonia inlet concentration (700 ppm) only after ≈500 s. This clearly indicates that ammonia is involved in adsorption–desorption processes at the catalyst surface. Along similar lines, upon the ammonia shut-off (t=1000 s) the reactor outlet NH_3 concentration slowly decreases with time due to the desorption of previously adsorbed ammonia. Complete desorption of NH_3 is not yet achieved after 2200 s, as shown by the lower value of area A_2 if compared with A_1. This indicates that part of the pre-adsorbed ammonia is strongly adsorbed on the catalyst surface. The NH_3 dynamic adsorption–desorption experiments were also performed at higher temperatures, in the range 220–400°C. On increasing the catalyst temperature, the variations in the ammonia outlet concentration during the adsorption step are faster and the amount of ammonia adsorbed on the catalyst surface is reduced, in line with the increased rates of the adsorption–desorption processes and with the exothermicity of the NH_3 adsorption.

Rectangular inlet step feeds were also performed with NO, and a typical result is shown in Fig. 1(B). It appears that the reactor outlet NO concentration curves closely resemble that of the inlet NO concentration: this indicates that NO does not appreciably adsorb onto the catalyst surface, in line with literature data [8]. Similar results have also been obtained over the binary V_2O_5/TiO_2 sample.

3.2. Transient kinetics of SCR of NO by NH_3

The dynamics of the SCR reaction has also been investigated. Accordingly, step feed experiments of NH_3, NO and O_2 have been performed, while keeping constant the concentration of the other reactants. Fig. 2(A) shows a typical result obtained upon performing step changes of the NH_3 reactor inlet concentration at 220°C in He+NO 700 ppm+O_2 1% v/v. The figure reports the evolution with time of NH_3, N_2 and NO concentrations.

Upon the NH_3 step feed at t=0 s, the NO reactor outlet concentration decreased due to the occurrence of the SCR reaction. The evolution with time of the ammonia, NO and N_2 concentrations shows different transient behaviors: the NH_3 concentration profile exhibits a dead time (≈250 s) and then slowly increases with time on stream to the new steady-state value, that is reached only after 800 s. On the other hand, the NO concentration trace does not show any dead time and decreases to its new steady-state value, reached after 300 s. The evolution with time of N_2 and of H_2O (not reported in Fig. 2) is specular to that of NO. No formation of other species (e.g. N_2O) was observed. It is worth of note that after 300 s, the reactor outlet NO concentration (and hence the NO conversion) is virtually constant, whereas the NH_3 concentration is still increasing. This is a clear indication of the fact that the NO conversion does not depend on the ammonia surface coverage (θ_{NH_3}) for θ_{NH_3} values above a characteristic 'critical' value.

A different transient behavior is observed upon the NH_3 shut-off (t=1000 s). Indeed whereas the NH_3 concentration dropped to zero, the NO concentration signal was not apparently affected; only after several minutes it began to increase up to the inlet concentration value. Again this indicates that the rate of the SCR reaction does not depend on θ_{NH_3} above a characteristic 'critical' value. The fact that NO is consumed even in the absence of gas-phase ammonia suggests that a 'reservoir' of adsorbed ammonia species available for the reaction is present on the catalyst surface.

Similar results were obtained by performing the NH_3 step-feed experiments at higher temperatures (280 and 350°C). In particular on increasing the reaction temperature: (i) the steady-state NO conversion is increased, (ii) the NH_3 and NO steady-state concentration levels are more rapidly reached; (iii) the 'dead time' in the variation of the NO concentration that is observed upon the ammonia shut-off (Fig. 2(A)) is reduced. Such temperature effects are in line with both the exothermicity of the NH_3 adsorption and with the increased rate of the surface reaction, which result in lower ammonia surface coverage. Accordingly at low θ_{NH_3} values the rate of NO consumption becomes dependent on the ammonia surface concentration, so that the evolution of NO closely follows that of NH_3.

The dynamic behavior of the SCR reaction upon step changes in the NO reactor inlet concentration has also been investigated. Fig. 2(B) show typical results obtained upon performing a rectangular step feed of NO at 493 K. Upon the NO step feed (t=0 s) the NH_3 reactor outlet concentration immediately decreases due to the occurrence of the SCR reaction, and a parallel evolution of N_2 and of water (not reported

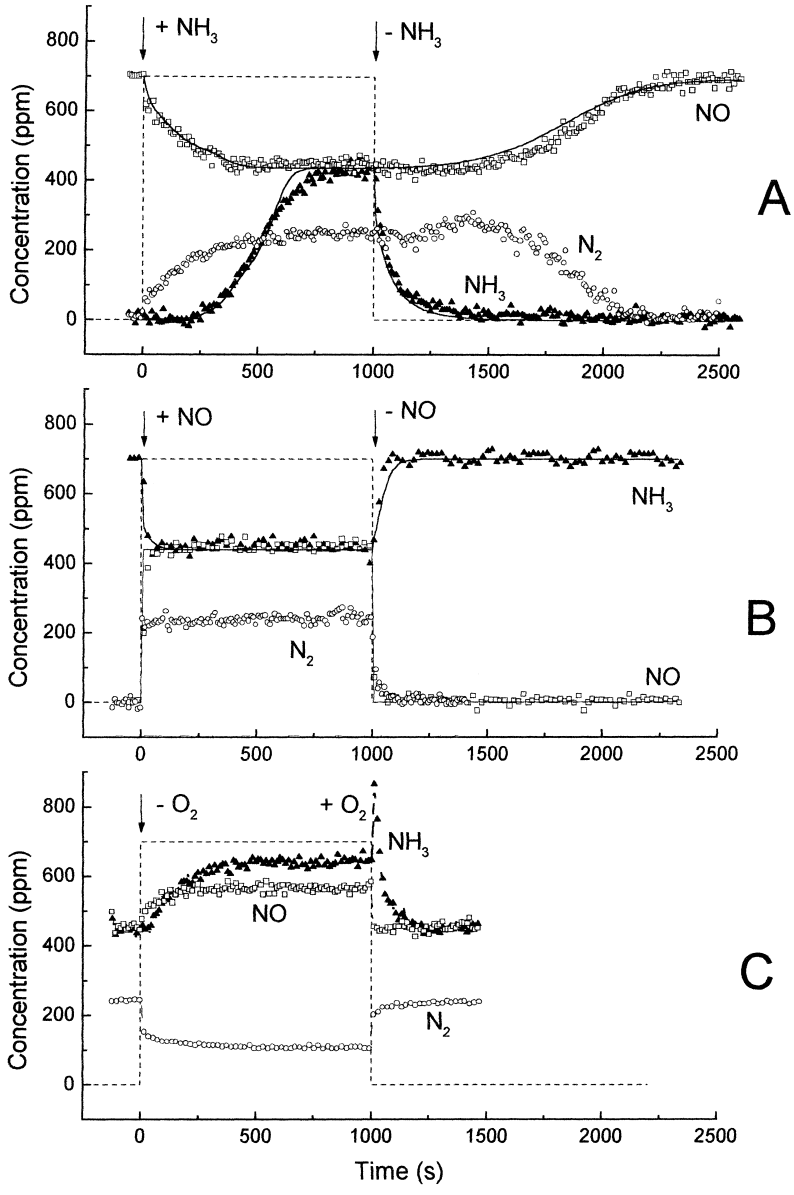

Fig. 2. Dynamic response upon step feed and shut-off of NH_3 (A), NO (B) and O_2 (C) on a model V_2O_5–WO_3/TiO_2 catalyst at 220°C. Dashed line: ideal step; solid lines: model fit.

in the figure) is observed. Along similar lines, upon the NO shut-off, the NO, NH_3 and N_2 reactor outlet concentration reach their steady-state values immediately. This picture significantly differs from that observed during the corresponding NH_3 step feed experiments reported in Fig. 2(A). The observed transient responses are typical of a reaction involving a strongly adsorbed species (NH_3) and a gas-phase or weakly adsorbed species (NO). Indeed, upon the NH_3 admission and shut-off (Fig. 2(A)), the NO (and NH_3) response is slow due to the fact that ammonia is involved in adsorption–desorption processes; on the other hand, the opposite is observed upon switches of NO (Fig. 2(B)). These data, along with the results of

the adsorption–desorption experiments shown in Fig. 1, are in line with the hypothesis of an Eley-Rideal mechanism for the SCR reaction involving strongly adsorbed NH_3 and gas-phase or weakly adsorbed NO.

Finally, the role of oxygen in the SCR reaction has been investigated. Fig. 2(C) shows that upon the O_2 shut-off at t=0 s the NH_3 concentration slowly increases to the new steady state value, whereas a more rapid transient behavior is observed for NO. It is also noted that in the absence of oxygen the NH_3 and NO steady-state levels differs, in line with the following stoichiometry of the SCR reaction:

$$4\,NH_3 + 6\,NO \rightarrow 5\,N_2 + 6\,H_2O \quad (2)$$

The NH_3 transient response could be explained by considering that, due to the low rate of the SCR reaction in the absence of oxygen, higher NH_3 surface coverage are expected and accordingly ammonia is adsorbed from the gas-phase until the new value is attained. On the other hand, the fact that the NO concentration does not reach the new steady-state value immediately, can be tentatively explained by considering that either adsorbed or catalyst lattice oxygen is available for the reaction so that the SCR reaction occurs via the faster reaction (1) instead of reaction (2). By assuming that only the vanadium catalyst lattice oxygen is involved in the reaction and that V^{5+} is reduced to V^{4+}, it is estimated that the reduction process involves roughly 3% of V^{5+}. This amount increases up to ~12% when the O_2 pulses are performed at 280°C.

Upon the O_2 re-admission at t=1000 s, NO rapidly reaches its new steady-state value whereas the reactor outlet NH_3 concentration at first increases and then decreases to the steady-state level. This particular behavior can be tentatively explained by considering that upon the catalyst reoxidation the temperature of the catalyst is increased, thus leading to the observed NH_3 desorption peak.

The data presented in Fig. 2 clearly show that the SCR reaction is faster in the presence of oxygen than in its absence, since a higher NO conversion is attained. This is in line with the well known promoting effect of the gas-phase oxygen on the SCR reaction. As pointed out in previous works [9–11] the SCR reaction occurs via a redox mechanism, which involves at first the catalyst lattice oxygen, followed by catalyst reoxidation by gas-phase oxygen. Oxygen accelerates the SCR reaction by increasing the rate of the reoxidation process, which in the absence of oxygen is carried out by NO. Several data have been reported in the literature concerning the possible role of oxygen in the NO oxidation and adsorption on the catalyst surface, but this feature seems to be more likely for Cu- [12–14], Cr- [15] or Mn-based [16,17] catalysts. As matter of facts, our data show that NO is not appreciably adsorbed on the catalyst surface even in the presence of oxygen (see Fig. 1), thus apparently ruling out a mechanism which involves NO oxidation and adsorption on the catalyst surface.

3.3. Kinetic analysis of the transient experiments

The results of the dynamic NH_3 adsorption–desorption and of the NH_3 and NO step feed experiments performed at different temperatures have been analyzed according to a dynamic one-dimensional heterogeneous PFR model and fitted by non linear regression to provide estimates of the relevant kinetic parameters. The O_2 transient experiments have not been analyzed and accordingly only qualitative information have been derived from these experiments. On the basis of diagnostic criteria, the influence of both intraparticle catalyst gradients and external mass transfer limitations were found negligible. Under these hypotheses, the unsteady mass balance of NH_3 on the catalyst surface and of NH_3 and NO in the gas-phase were written (Eqs. (1–3) of Table 1, respectively), where C_{NH_3} and C_{NO} represent the NH_3 and NO gas-phase concentration, respectively; r_a, r_d and r_{NO} the rate of adsorption, desorption and of NO consumption, respectively; v is the interstitial gas velocity, z the reactor axial coordinate and Ω the catalyst NH_3 adsorption capacity. On the basis of

Table 1
Unsteady mass balances of NH_3 on the catalyst surface (1) and of NH_3 (2) and NO (3) in the gas phase

$$\frac{\partial \theta_{NH_3}}{\partial t} = r_a - r_d - r_{NO} \quad (1)$$

$$\frac{\partial C_{NH_3}}{\partial t} = -v\frac{\partial C_{NH_3}}{\partial z} + \Omega(r_d - r_a) \quad (2)$$

$$\frac{\partial C_{NO}}{\partial t} = -v\frac{\partial C_{NO}}{\partial z} - \Omega\, r_{NO} \quad (3)$$

preliminary fits of the experimental data, it was found that the NH_3 adsorption occurs via a non-activated process, described by the rate expression $r_a = k_a^o C_{NH_3}(1-\theta_{NH_3})$, with k_a^o=constant. An activated kinetic rate expression was instead used for NH_3 desorption ($r_d = k_d^o \exp(-E_d/RT)\theta_{NH_3}$). Different dependence of E_d on θ_{NH_3} have been used, including E_d=constant (Langmuir) and more complicate expressions that take into account the catalyst surface heterogeneity. These included Temkin-type ($E_d = E_d^o(1-\alpha\theta_{NH_3})$), modified Temkin-type ($E_d = E_d^o(1-\alpha\theta_{NH_3}^{\sigma})$) and Freundlich ($E_d = E_d^o \exp(-\alpha\theta_{NH_3})$) coverage dependence of E_d, along with more complicate empirical expressions. Also, different rate expressions have been tested for the SCR reaction (r_{NO}). These always include a first order dependency on C_{NO}, and various order dependencies with respect to θ_{NH_3}, including first-order ($r_{NO} = k_{NO}C_{NO}\theta_{NH_3}$) and 'modified' θ kinetics ($r_{NO} = k_{NO}C_{NO}\theta^*_{NH_3}[1-\exp(-\theta_{NH_3}/\theta^*_{NH_3})]$). In this case the rate of reaction is considered independent on θ_{NH_3} above a critical NH_3 surface concentration value ($\theta^*_{NH_3}$), in line with the results of the NH_3 step addition experiments reported in Fig. 2(A). Nice fits of the experimental data for both the binary and the ternary catalysts could be achieved by using a Temkin-type NH_3 desorption kinetics (the Langmuir approach fails in quantitatively describing the experimental data) and the 'modified' θ kinetics for r_{NO}. A typical data fit obtained in the case of the ternary sample is reported as solid line in Figs. 1 and 2, whereas the estimates of the kinetic parameters used in the data fit are reported in Table 2, along with those corresponding to the binary sample. The optimal parameter estimates yield an activation energy for NH_3 desorption at zero coverage (E_d^o) close to 25 kcal/mol for both catalysts. The slightly higher value of the catalyst capacity (Ω=270 vs. 209 mol_{NH_3}/m^3) of the ternary catalyst may be due to its higher specific surface area with respect to the V_2O_5/TiO_2 binary sample (80 vs. 46 m^2/g). An activation energy for the SCR reaction close to 15 kcal/mol has been estimated for both catalysts, in agreement with literature values [18].

Table 2
Estimates of the kinetic parameters for the SCR reaction over V_2O_5/TiO_2 and V_2O_5–WO_3/TiO_2 catalysts leading to the fits reported in Figs. 1 and 2 (solid lines). Rate equations: $r_a = k_a^o C_{NH_3}(1-\theta_{NH_3})$; $r_d = k_d^o \exp(-E_d/RT)\theta_{NH_3}$ with $E_d = E_d^o(1-\alpha\theta_{NH_3})$; $r_{NO} = k_{NO}C_{NO}\theta^*_{NH_3}[1-\exp(-\theta_{NH_3}/\theta^*_{NH_3})]$

Parameters	V_2O_5–WO_3/TiO_2	V_2O_5/TiO_2
k_a^o (m^3/mol s)	0.614	0.820
k_d^o (l/s)	1.99×10^5	3.67×10^6
E_d^o (kcal/mol)	23.4	25.8
α	0.448	0.310
Ω (mol/m^3)	270	209
k_{NO}^o (m^3/mol s)	8.39×10^5	1.08×10^6
E_{NO} (kcal/mol)	14.2	16.0
$\theta^*_{NH_3}$	0.108	0.076

3.4. Relevance to the study of kinetic and mechanistic aspects of the SCR reaction

The results of the dynamic study previously reported are in many respect relevant to the study of both kinetic and mechanistic aspects of the SCR reaction. It is worth emphasizing that these aspects could not be collected under steady-state conditions, and points out that dynamic conditions are best suited for mechanistic study of complex reactions. In particular, the NH_3 dynamic adsorption–desorption study demonstrated that ammonia is strongly adsorbed on the catalyst surface and that surface heterogeneity must be considered when describing the NH_3 interaction with the catalyst surface. This is in line with various characterization data showing the presence of different adsorption sites for ammonia, including Lewis and Brønsted acid sites [19,20]. Similar results have been obtained over both the binary and the ternary catalyst, thus eventually indicating that the acid characteristics of the two samples, with respect to the NH_3 adsorption–desorption, are similar.

The study of the dynamics of the SCR reaction showed that the $DeNO_x$ reaction has a complex kinetic dependence on the ammonia surface coverage. Indeed the rate of the SCR reaction is a function of the ammonia surface concentration for NH_3 coverage below a characteristic 'critical' value, whereas a much weaker dependence exists at high coverage. As already suggested above, this indicates that a 'reservoir' of adsorbed ammonia species is present on the catalyst surface. The ammonia 'reservoir' is likely associated with the W and Ti surface species that are exposed at the catalyst surface in the case of the sub-

monolayer samples investigated in the present study. These species effectively adsorb NH_3, but their reactivity in the SCR reaction is limited [8,21] with respect to the V sites. Accordingly, these Ti- and W-bonded adsorbed ammonia species do not act as 'spectators' in the SCR reaction but can be involved in the NO consumption via desorption and subsequent fast readsorption over available reactive V-sites, in line with the results of the kinetic analysis.

The dynamic behavior of the SCR reaction could be nicely fitted by assuming a first order dependence on NO and a more complex dependence on the ammonia surface concentration (zero-order at high NH_3 coverage and first-order below a 'critical' coverage $\theta^*_{NH_3}$). This suggests that the catalyst active sites represent only a fraction of the total adsorption sites for ammonia. As a matter of fact, in line with the hypothesis of V being the active element in the SCR reaction, it has been found that the 'critical' NH_3 coverage $\theta^*_{NH_3}$ is of the same order of magnitude of the catalyst V coverage. An important implication of the mechanistic considerations reported above is that in developing a kinetic model a distinction should be made between ammonia 'adsorption' and 'reaction' sites. Finally, the analysis of the parameter estimates obtained over both the binary and the ternary samples leads to additional implications concerning the steady-state kinetics of the SCR reaction. Indeed, being at steady-state $r_a = r_d + r_{NO}$, it follows that $r_a \approx r_d$ (i.e. NH_3 adsorption–desorption equilibrium) only if r_{NO} is negligible with respect to r_d ($r_{NO} \ll r_d$). From the values of the kinetic parameters reported in Table 1 it is possible to estimate the r_d/r_{NO} ratios at different reactor axial position, different reaction temperatures and for different catalysts. It has been found that the values of the r_d/r_{NO} ratio do not change significantly between the inlet and the outlet of the reactor, and decrease upon increasing the temperature. The r_d/r_{NO} ratio is greater than 1 at 553 K and in the case of the less active vanadia/titania catalyst ($r_d/r_{NO} \sim 10$) but it is close to 1 at the same temperature over the most active vanadia–tungsta/titania catalyst. This demonstrates that the assumption of equilibrated ammonia adsorption, often used in the derivation of steady-state kinetic expressions for the SCR [22], is in fact not always appropriate, and specifically at high temperatures and over very active catalysts, where not a single rate controlling step can be identified.

4. Conclusions

The major results of our study can be summarized as follows:

1. Surface heterogeneity must be considered to describe the kinetics of NH_3 adsorption–desorption on TiO_2-supported V_2O_5-based catalysts: a model assuming a non-activated NH_3 adsorption process and a Temkin-type coverage dependence of E_d nicely represents the dynamic data.
2. In contrast to NH_3, NO does not adsorb appreciably on the catalyst surface, in line with an Eley-Rideal mechanism for the SCR reaction.
3. The rate of the $DeNO_x$ reaction is virtually independent on the NH_3 surface concentration for θ_{NH_3} above a characteristic 'critical' value that is of the same order of magnitude of the V surface coverage. This is explained by assuming that a 'reservoir' of adsorbed NH_3 species (likely on W and Ti sites) is present on the catalyst surface and is available for the reaction via desorption and subsequent fast readsorption over reactive V-sites, in line with the results of the kinetic analysis.
4. A comparison among the estimates of the adsorption, desorption and reaction rates calculated at different reactor axial position, temperatures and catalysts indicates that the assumption of equilibrated ammonia adsorption under steady-state $DeNO_x$ conditions is likely incorrect, specifically at high temperatures and over active catalysts.

References

[1] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[2] P. Forzatti, L. Lietti, Heter. Chem. Rev. 3(1) (1996) 33.
[3] S.L. Andersson, P.L.T. Gabrielsson, C.U.I. Odenbrand, AIChE. J. 40(11) (1994) 1911.
[4] A. Noskov, L. Bobrova, G. Bunimovich, O. Goldman, A. Zagoruiko, Y. Matros, Catal. Today 27 (1996) 315.
[5] H. Kobayashi, M. Kobayashi, Catal. Rev. Sci. Eng. 10 (1974) 139.
[6] L. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello, F. Bregani, J. Catal. 155 (1995) 117.
[7] L. Lietti, I. Nova, S. Camurri, E. Tronconi, P. Forzatti, AIChE. J. 43(10) (1997) 2559.
[8] T.Z. Srnak, J.A. Dumesic, B.S. Clausen, E. Törnqvist, N.Y. Topsøe, J. Catal. 135 (1992) 246.
[9] L. Lietti, P. Forzatti, F. Berti, Catal. Lett. 41 (1996) 35.

[10] L. Lietti, P. Forzatti, F. Bregani, Ind. Eng. Chem. Res. 35(11) (1996) 3884.
[11] L. Lietti, P. Forzatti, J. Catal. 147 (1994) 241.
[12] G. Ramis, Yi Li, G. Busca, M. Turco, E. Kotur, R.J. Willey, J. Catal. 157 (1995) 523.
[13] G. Centi, S. Perathoner, P. Biglino, E. Giamello, J. Catal. 152 (1995) 75.
[14] G. Centi, S. Perathoner, P. Biglino, E. Giamello, J. Catal. 152 (1995) 93.
[15] H. Schneider, U. Scharf, A. Wokaun, A. Baiker, J. Catal. 147 (1994) 545.
[16] F. Kapteijn, L. Singoredjo, M. van Driel, A. Andreini, J.A. Moulijn, G. Ramis, G. Busca, J. Catal. 150 (1994) 105.
[17] F. Kapteijn, L. Singoredjo, A. Andreini, J.A. Moulijn, Appl. Catal. B: Environ. 3 (1994) 173.
[18] W.C. Wong, K. Nobe, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 564.
[19] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Appl. Catal. 64 (1990) 259.
[20] N.-Y. Topsøe, J. Catal. 128 (1991) 499.
[21] L. Lietti, Appl. Catal. B: Environ. 10 (1996) 281.
[22] J.A. Dumesic, N.-Y. Topsøe, T. Slabiak, P. Morsing, B.S. Clausen, E. Tornqvist, H. Topsøe, in: L. Guczi, et al. (Eds.), New Frontiers in Catalysis, Elsevier, Amsterdam, 1992, 1325 pp.