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Experimental Investigation of the SCR of NO_x in a Simulated Moving Bed Reactor

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The experimental investigation of the Selective Catalytic Reduction (SCR) of NO_x with NH_3 in a Simulated Moving Bed (SMB) reactor realized by means of a network of three catalyst beds with periodical variation of the feed position is dealt with. The influence of the main operating parameters, namely, the inlet flow rate, the switching frequency, and the working temperature, has been investigated, as well as the responses of this device to disturbances in the feeding. A simple one-dimensional (1-D) model has been validated by means of the comparison with the experimental results. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3146–3154, 2006
Keywords: selective catalytic reduction, NO_x removal, simulated moving bed reactor, reactor network, chromatographic reactor

Introduction

Multifunctional reactors allow for coupling several operations (chemical reaction, separation, and/or heat exchange process) into a single equipment, thus improving yield and productivity, and reducing investment and operation costs, with respect to more traditional reactor configurations. The reverse-flow reactor (RFR), that is, a fixed-bed reactor with periodical reversal of the feed direction, is a well known example of a multifunctional reactor where regenerative heat exchange is coupled with chemical reaction. This allows, for example, the autothermal combustion of lean VOC-air mixtures as the periodical reversal of the feed flow direction traps the heat of combustion in the catalytic bed.[1,2]

The Simulated Moving Bed (SMB) reactor is another configuration that can be used to achieve multifunctional operation. Since the end of the 90s, Barresi's group at the Politecnico di Torino investigated a network of N catalytic reactors with periodical variation of the feed position, focusing attention on gas-solid catalytic reactions, namely, the catalytic combustion of lean VOC mixtures,[3,4] low pressure methanol synthesis,[5] and synthesis gas production.[6] The main motivation for such researches is that in the SMB reactor, the flow direction is never changed, thus avoiding the occurrence of wash out, that is, the emission of unconverted reactants occurring in the RFR when the flow direction is reversed. In all these studies, a compact approach was proposed, and all the N units are used at all times. In the first interval the reactants are fed through unit 1, whereas the products exit at the end of unit N; in the second interval the reactants are fed through unit 2, whereas the products exit at the end of unit 1; and so on. The feed and the exit streams are adjacent in this configuration. Sheintuch and Nekhamkina[7] proposed a different configuration, where only $N-1$ units are used at all times. In the first interval the reactants are fed through unit 1 and the products exit from unit $N-1$; in the second interval the flow enters at unit 2 and exits from unit N; and so on. This approach requires fewer valves and tubes, but allows a less efficient use of the catalyst.

Beside coupling chemical reaction and heat exchange, a great deal of attention has been paid to the possibility of coupling chemical reaction and adsorptive separation: the continuous separation of products can drive a reversible reaction to near completion as it suppresses the rate of the reverse reaction and, at the same time, high purity products are obtained, thus resulting in the so-called chromatographic reactor. Chromatographic separations can be achieved in the RFR if the reactor is packed with an adsorbent, or with a mixture of adsorbent and catalyst, with a high adsorption capacity toward a reactant and

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low toward a product, so that the periodic switching of the feed traps the strongly adsorbed reactant inside the reactor. The Selective Catalytic Reduction (SCR) of NO_x with ammonia in the presence of a catalyst that strongly adsorbs the ammonia was proposed in the past[8-10] as a process that can be carried out in an RFR taking advantage of this mode of reactor operation. Some authors[9,11] proposed various solutions to avoid wash out of unconverted ammonia, but, in our mind, the most effective and efficient solution is the SMB reactor made of two or three reactors connected in a closed sequence and with a set of valves that enable changing the feed position, thus simulating the behavior of a moving bed and achieving a sustained dynamic behavior.[12,13]

In this article an experimental setup for the investigation of the SCR of NO_x in an SMB made of three reactors is described, and the results are compared to the simulations carried out by means of a simple one-dimensional model. To our knowledge, this work represents also the first attempt to investigate a catalytic reaction in an SMB by means of experiment, thus allowing for the validation of the modeling results. The article is structured as follows: first we describe the experimental apparatus; then fundamentals of the mathematical model are given; and finally, the validation is given, with the results of the experimental investigation.

Experimental Apparatus

A network of three reactors has been built in our labs at the Politecnico of Torino. Each reactor is made up of a tube of stainless steel (AISI 316), with a diameter of $2.54 \cdot 10^{-2}$ m and a length of $15 \cdot 10^{-2}$ m, and contains $7.5 \cdot 10^{-2}$ m of a monolith (64 CPSI) supporting the catalyst for the SCR reaction. The commercial zeolite based NO_xCAT^{TM} ETZ catalyst by Engelhard has been used. The experimental investigation has been carried out in isothermal conditions in order to focus on the impact of the operation parameters on the dynamic features caused by the trapping of one reactant in the reactor, thus neglecting the dynamic of the heat wave. To this purpose, the three reactors are placed in an oven designed to ensure a uniform temperature all along the reactors. Catalyst temperature was measured and controlled: the temperature can be varied until a maximum value of 400°C; the range 200-350°C has been investigated. Five three-way valves are required to change the feed position along the sequence of the three reactors. Figure 1 shows the layout of the system and the valves required: acting on them it is possible to change periodically the reactor sequence from the initial 1–2-3 to 2–3-1 and finally to 3–1-2, as is shown in the Figure where the thicker lines evidence the gas path in the three steps of each period. For the calculation of the kinetic constants of adsorption, desorption, and reduction step, the same apparatus has been employed, using a single reactor and venting.

In both setups the two reactants, namely, NO and NH_3, come from two cylinders: one contains NO (950 ppmV) and Ar, while the other contains NH_3 (969 ppmV), Ar, and also O_2 (2%), which is required by the SCR reaction:

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

Two mass flow meters and controllers allow for setting and controlling the desired flow rate and composition of the process feed; total flow rate can vary in the range 0-4 Nl min^{-1}, while the inlet NO and NH_3 concentrations are equal to 450 and 425 ppmV, respectively.

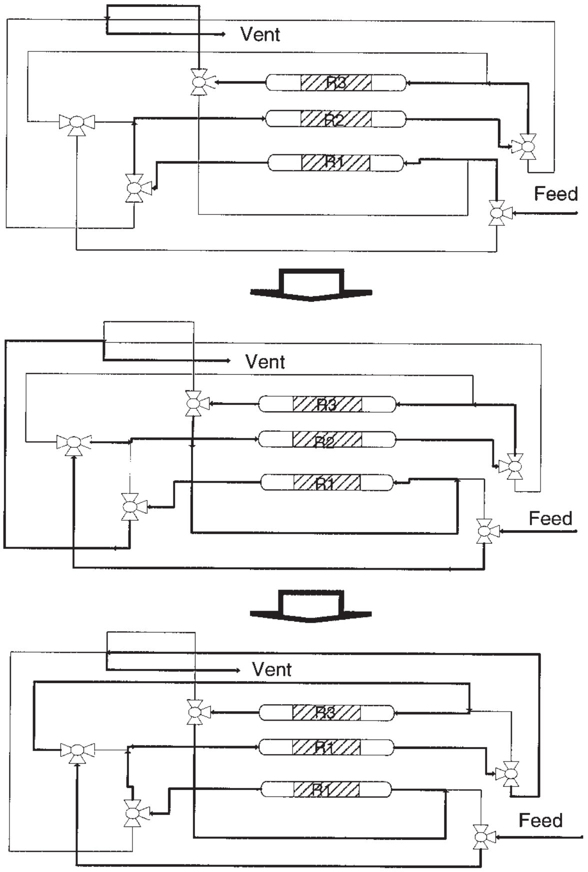

Figure 1. Experimental rig.

Products of reaction are measured continuously by means of a quadrupole mass spectrometer (QMS). As it is not trivial to obtain reliable quantitative measures from a QMS, the procedure followed during the measurements will be described in detail in the Appendix.

Mathematical Modeling

A one-dimensional heterogeneous mathematical model is required to analyze the experimental results. An Eley-Rideal mechanism is used to describe the reaction between NO (A) in the gas phase and the ammonia (B) adsorbed on the catalyst:

$$B + S \rightarrow B_S \qquad (2)$$

$$A + B_S \rightarrow C \qquad (3)$$

The reduction reaction is generally considered to be of first order with respect to each reactant:

$$r_{red} = -k_{red} c_A^* \theta_B \Omega \qquad (4)$$

where θ_B is the ammonia surface coverage and c_A^* is the concentration of reactant A at the gas-solid interface and Ω is the catalyst capacity; O_2 is considered to be in great excess and it is treated as constant. In some articles,[14,15] the rate of reduction appeared to be essentially independent of the ammonia surface coverage above a critical NH_3 surface concentration (θ_B^ν) and was described by the following relationship:

$$r_{red} = -k_{red} c_A^* \theta_B^\nu (1 - e^{\theta_B/\theta_B^\nu})\Omega \tag{5}$$

The same relationship was adopted in this work on the basis of the results obtained in the kinetic preliminary tests. The adsorption rate of ammonia on the catalyst surface is assumed to be proportional to the ammonia concentration in the gas phase and to the free fraction of surface sites:

$$r_{ads} = k_{ads} c_B^* (1 - \theta_B)\Omega \tag{6}$$

while the rate of desorption is assumed to be proportional to the concentration of the adsorbed specie:

$$r_{des} = k_{des} \theta_B \Omega \tag{7}$$

A Temkin-type desorption kinetics, where the activation energy for desorption is a function of the surface coverage, is generally assumed, and it has been adopted also in this case:

$$E_{a,des} = E^{\zeta}_{a,des}(1 - \beta\theta_B^\sigma) \tag{8}$$

An Arrhenius type dependence of the kinetic constants k, k_{ads}, and k_{des} from the temperature is stated:

$$k_{red} = k_{0,red} e^{-(E_{a,red}/RT_S)};\; k_{ads} = k_{0,ads} e^{-(E_{a,ads}/RT_S)};\; k_{des} = k_{0,des} e^{-(E_{a,des}/RT_S)} \tag{9}$$

The system of partial differential equations that describes the process dynamics is the following:

- gas phase mass balances:

$$\frac{\partial c_A}{\partial t} = -\nu \frac{\partial c_A}{\partial x} + h_A a_\nu (c_A^* - c_A) \tag{10}$$

$$\frac{\partial c_B}{\partial t} = -\nu \frac{\partial c_B}{\partial x} + h_B a_\nu (c_B^* - c_B) \tag{11}$$

The value of $c_A{}^*$ and $c_B{}^*$, the gas concentration at the interface, can be calculated from the mass balance at the interface, assuming that there is no accumulation at the gas interface:

$$-h_A a_\nu (c_A^* - c_A) = r_{red} \tag{12}$$

$$-h_B a_\nu (c_B^* - c_B) = (r_{ads} - r_{des}) \tag{13}$$

- solid phase mass balance:

$$\Omega \frac{\partial \theta_B}{\partial t} = r_{ads} - r_{des} - r_{red} \tag{14}$$

Heat- and mass-transfer coefficients have been calculated using the asymptotic solution for a fluid with fully developed concentration and temperature profiles.[16] Inlet composition of the gases is considered constant and equal to the feeding value, and the initial concentration of ammonia adsorbed on the catalyst surface is equal to 0 in all the runs; the temperature is considered to be constant and pressure losses are assumed to be negligible.

The system of partial differential equations, Eqs. 10-14, has been solved by discretizing the domain of the spatial variables into a grid of 100 points, equally spaced, thus obtaining a grid-independent solution. The MatLAB solver ode15s, which is a quasi-constant implementation of the Numerical Differentiation Formulas in terms of Backward Differences,[17] has been used to solve the system; the relative and absolute tolerances have been set equal to the square root of the working machine precision.

Experimental Investigation

Kinetic study of the catalytic reaction

The kinetic parameters of the adsorption, desorption, and reduction reactions, as well as the catalyst capacity, are required in order to investigate the performance of the reactor network. As a consequence, preliminary runs have been carried out to get these values. The application of transient methods to the study of kinetic and mechanistic aspects of heterogeneous catalytic reactions is rapidly growing nowadays.[14,18,19] These methods consist of imposing perturbations to the reacting system (such as changes of the inlet reactant concentration or catalyst temperature), while continuously monitoring the outlet transient response. The characteristics of the transient response reflect the nature of the sequence of steps underlying the kinetics of the reaction: accordingly, these methods are able to provide, in principle, mechanistic and kinetic evidence that cannot be collected under steady-state conditions. By imposing step-wise changes in the inlet NO and/or NH_3 concentration, the dynamics of SCR reaction can thus be investigated and mechanistic aspects of the reaction can be clarified. Also, the adsorption/desorption of the reactants could be investigated separately from their surface reaction, thus gaining detailed information on each single step of the reaction. Quantitative kinetic indications can be obtained by analyzing the results according to dynamic models of the reacting system.[18]

The transient NH_3 adsorption/desorption study was performed in the previously described setup by imposing step-wise perturbations of the NH_3 reactor inlet concentration at various temperatures in flowing Ar, while maintaining the overall flow rate constant. Diagnostic blank experiments with no catalyst in the reactor were also performed: no evidence of homogeneous gas-phase reactions was detected.

Typical results obtained upon imposing a step change to the inlet concentration of NH_3 are presented in Figure 2 (upper graph, symbols): upon increasing the NH_3 inlet concentration, the ammonia outlet concentration shows a dead time and then a rapid increase up to the value of the inlet concentration, which is reached after about 2500 s. The amount of NH_3 adsorbed onto the catalyst surface has been calculated according to Lietti et al.[14] When the ammonia feeding is stopped, the outlet NH_3 concentration shows a tail due to the desorption of the previously adsorbed ammonia. NH_3 adsorption/desorption

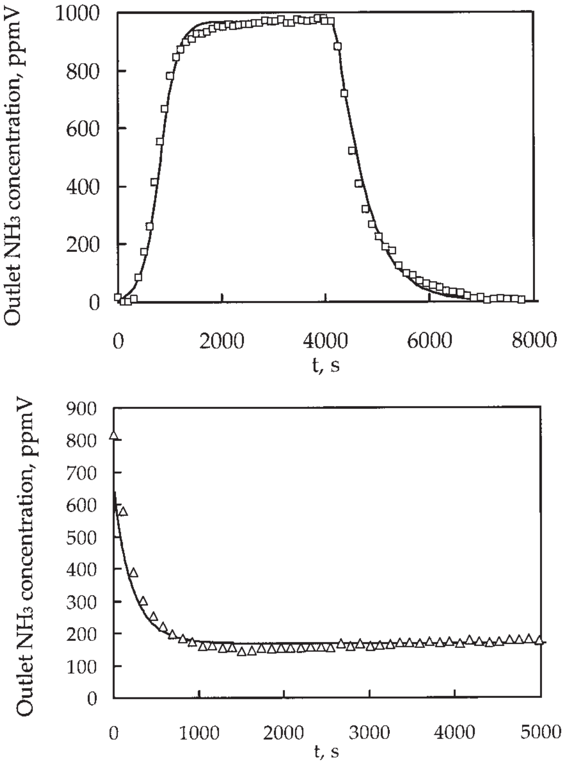

Figure 2. Upper graph: Outlet ammonia concentration during an adsorption/desorption experiment; Lower graph: Outlet ammonia concentration during a reduction experiment.

Upper graph: T_S = 320°C; during the adsorption run a flow rate of 2 Nl min^{-1} of a mixture containing 969 ppmV of NH_3 in Ar is fed to the reactor, while in the desorption run a flow rate of 1 Nl min^{-1} of Ar is fed to the reactor.

Lower graph: T_S = 320°C; feed composition: 969 ppmV of NH_3, 950 ppmV of NO, 1% O_2, difference Ar, feed flow rate: 2 Nl min^{-1}.

experiments were performed at different temperatures in the range 500-650 K; the data are not reported here for brevity. In order to gain quantitative information on the NH_3 adsorption-desorption characteristics, the whole set of experimental data has been analyzed according to the previously described mathematical model. In line with previous dynamic analyses,[18,20] a Temkin-type NH_3 desorption kinetic has been considered. The MATLab routine FMINSEARCH, which implements a simple simplex method that does not use numerical or analytical gradients,[21] has been used to calculate the kinetic parameters that allow for the best fit with the experimental values of concentration. An example of data fit is reported as a solid line in Figure 2 (upper graph): it appears that the goodness of the fit is satisfactory and that the most relevant features of the experiment are reproduced.

Similar experiments have been carried out to find out the kinetic parameters of the reduction reaction. In this case, both NO and NH_3 are fed to the reactor: experiments were performed at different temperatures in the range 500-650 K and with various values of the flow rate. Before performing this type of experiments, the catalyst bed was saturated with ammonia; this allowed the calculation of the parameters required for the calibration of the QMS. Figure 2 (lower graph, symbols) shows an example of the results that have been obtained during this type of run. In order to get a good fit with the experimental results, the rate of reduction is supposed to be independent of the ammonia surface coverage above a critical NH_3 surface concentration (θ_B^ν), as has been stated in Eq. 5. Results of the fitting are given as solid lines in Figure 2 (lower graph), proving the adequacy of the adopted model for the description of the catalyst. The results of this study are summarized in Table 1.

Experimental investigation of the SMB reactor

The behavior of the SMB reactor made up of three reactors with periodically varying feeding position has been investigated by means of experiments for various working temperatures, feed flow rates, and compositions. All the reactors of the network contain the same amount of catalyst (each monolith is $7.5 \cdot 10^{-2}$ m long). The results are given in terms of (integral) mean concentration over a complete period of the operation. Experimental values are always compared with modeling predictions obtained using the parameters of Table 1 and setting the values of the operating parameters (temperature, flow rate, inlet concentration, switching time) to those used in the experimental run.

Figure 3 shows the results obtained when the system temperature is maintained at three different values (250°C, 300°C, 350°C); the outlet mean value of NO and of NH_3 is given (the switching time is maintained constant and equal to 60 s). In each run the catalyst has no NH_3 adsorbed at the beginning (during the heating of the catalyst Ar is fed in order to remove the NH_3 remained adsorbed in the previous run). As it can be expected, the higher the temperature of the system, the lower are the emissions of NH_3 and of NO (of course, at lower temperature it would be necessary to have a larger catalytic section to ensure complete conversion). At the beginning of the experiment, the outlet NO concentration is quite high, due to the low concentration of ammonia adsorbed onto the catalyst, but the NH_3 slip is avoided; of course, if the conversion of NO is too low, when the catalyst has been saturated slip can occur. The mathematical model adequately reproduces both the dynamic evolution in the transient and the steady-state values.

The influence of the feed flow rate at fixed t_c is shown in Figure 4. The lower is the flow rate, the lower are the concentrations of NO and of NH_3 in the product stream (due to the higher contact time), but the higher is the time interval required to get the steady-state value. Also in this case, the mathematical

Table 1. Values of the Kinetic Parameters of the Adsorption, Desorption, and Reduction Reaction Calculated by Means of Fitting with the Experimental Results

$k_{0,red}$, s^{-1}	$3.23 \cdot 10^5$
$E_{a,red}$, J mol^{-1}	77500
θ_B^ν	0.013
$k_{0,ads}$, m^3 mol^{-1} s^{-1}	0.887
$E_{a,ads}$, kJ mol^{-1}	9.54
$k_{0,des}$, s^{-1}	$2.43 \cdot 10^5$
$E_{a,des}^\zeta$, J mol^{-1}	113970
β	0.163
σ	1.0
Ω, mol m^{-2}	130

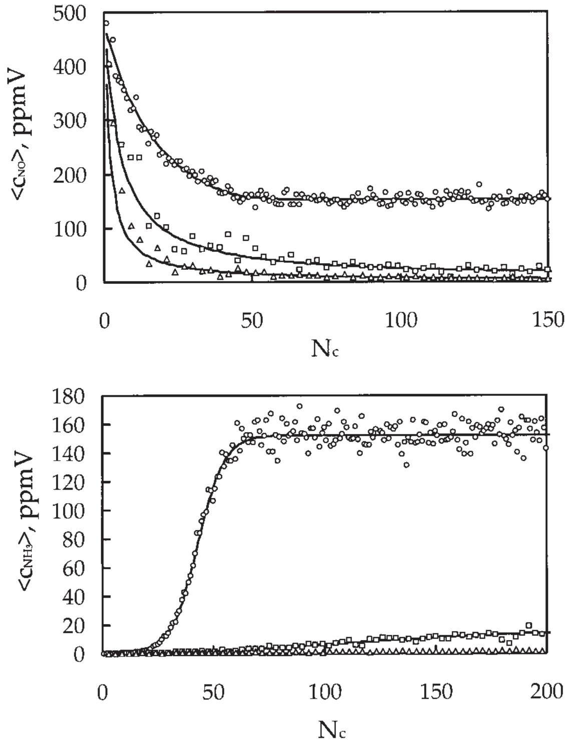

Figure 3. Comparison between the experimental values (symbols) and the model predictions (solid lines) of the mean outlet concentration of NO (upper graph) and of NH_3 (lower graph) for various temperatures of the SMB.

o: T = 250°C, □: T = 300°C, △: T = 350°C. Operating conditions: feed composition: 485 ppmV of NH_3, 475 ppmV of NO, 1% O_2, difference Ar; feed flow rate: 2 Nl min^{-1}, t_c = 60 s.

model adequately reproduces both the dynamic evolution in the transient and the steady-state values.

The SMB is known to respond much more efficiently than a fixed bed working in steady-state to any perturbations in the pollutant feed rate and/or concentration. In particular, if the operation is carried out using a fixed concentration of NH_3, the adsorbed NH_3 may be used to remove NO_x when its concentration is higher than the stoichiometric value; similarly, if the concentration of NO_x is lower than the stoichiometric, the catalyst may adsorb the NH_3 in excess. In order to point out the behavior of the SMB towards changes in the feed composition, we have considered two extreme situations: in the first, NO feed is stopped; in the second, the flow of NH_3 is stopped; in both cases the system is initially in the PSS condition and the switching time is not changed, in order to highlight the robustness of these devices to face against disturbances without any control action.

Figure 5 (upper graph) shows the mean outlet NH_3 concentration as a function of the number of cycles after the stop in NO feeding; experimental results and model predictions are given for two values of the switching time. When the switching time is equal to 600 s, it takes a few (a couple of) cycles (which means about 1 h) to have in the exit stream the same concentration of the feeding, and thus no NO conversion. The same situation takes place when the switching time is equal to 60 s; it takes about 1 hour (in this case 20 cycles) to extinguish the reaction. The same conclusions come from Figure 5 (lower graph) when the opposite situation is studied, that is, a stop in NH_3 feeding. Also in this case, experimental results and model predictions are given for two values of the switching time (60 s and 600 s) and, again, the same behavior of the reactor is shown.

The time evolution of the outlet NH_3 concentration during a period, when the PSS has been reached, is shown in Figure 6 for two values of the switching time. When the reactor is operated at low t_c (60 s), the outlet concentration of ammonia is almost constant and lower than the value obtained when the switching time is higher (600 s); moreover, at high t_c, the outlet concentration of ammonia decreases with time during the period. The role played by the switching time is much more important when non-isothermal operation is investigated. As has been pointed out by Fissore et al.,[12] even if the adiabatic temperature rise in NO_x removal is usually of the order of 10-20 K, the temperature rise in an SMB will be a multiple of this value, thus allowing autothermal operation when low temperature gas is fed to the reactor. In these conditions, the choice of the switching time will be affected also by the dynamics of the heat wave, and too long switching times should be avoided as they lead to reaction extinction, due to the heat removal from the catalyst.

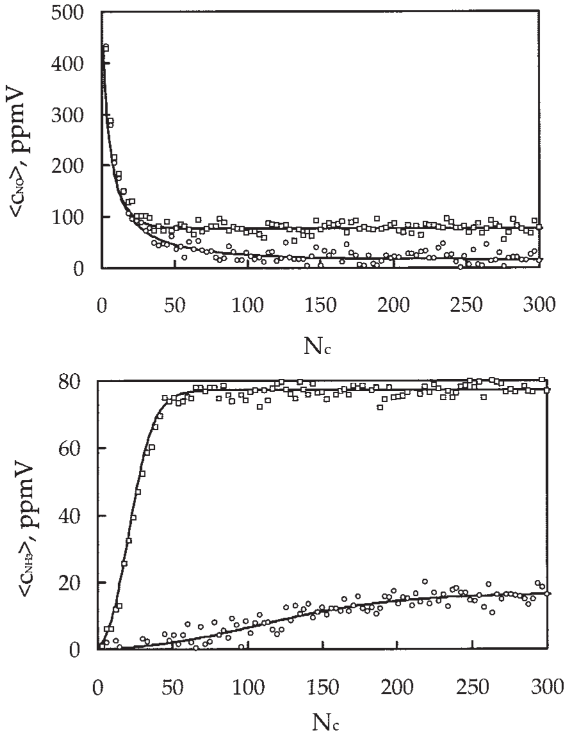

Figure 4. Comparison between the experimental values (symbols) and the model predictions (solid lines) of the mean outlet concentration of NO (upper graph) and of NH_3 (lower graph) for various feed flow rate.

o: 2 Nl min^{-1}, □: 4 Nl min^{-1}. Operating conditions: feed composition: 485 ppmV of NH_3, 475 ppmV of NO, 1% O_2, difference Ar; temperature: 300°C, t_c = 60 s.

Conclusions

The feasibility of the Selective Catalytic Reduction of NO_x with ammonia in a SMB realized with a network of three reactors with periodical variations of the feeding position has been demonstrated by means of numerical simulations and experimental investigation. This device has been shown to be effective in avoiding the emissions of ammonia (whose level is subject to stricter limits than for NO_x), besides fulfilling the requirements on NO_x conversion. Isothermal operation has been investigated in order to focus on the consequences of the trapping of one reactant, thus neglecting the dynamic of the heat wave. The influence of the working temperature, of the feed flow rate, of the feed composition, and of the switching time on the composition of the product stream has been assessed by means of simulations and experiments. Finally, the response of the SMB to disturbances in the feed composition has been investigated, evidencing the robustness of the SMB and the ability to face against perturbations in the feeding for a long time interval without any control action.

Future work should concern the investigation of the SMB operated in nonisothermal operation, thus focusing on the impact of the heat balance on the results and confirming the preliminary results obtained by simulation.

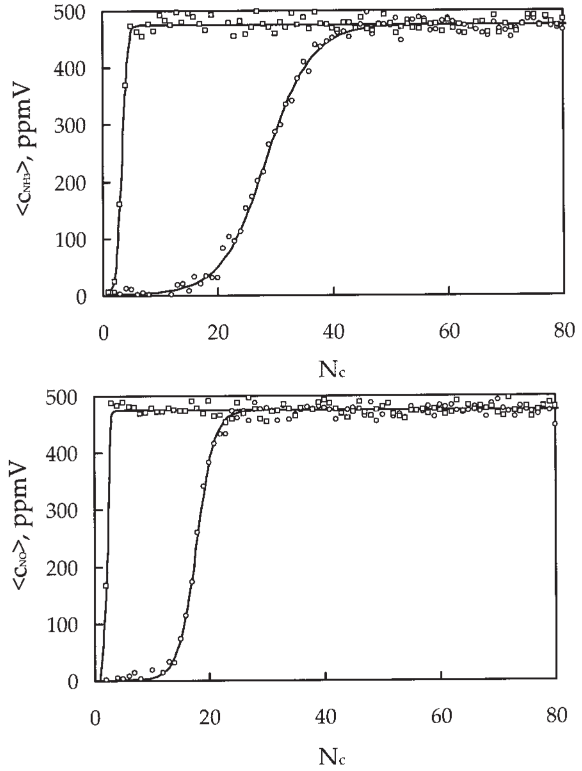

Figure 5. **Upper graph: Response to a stop in the feed of NO; Lower graph: Response to a stop in the feed of NH_3.**

Upper graph: Feed composition: 485 ppmV of NH_3, 1% O_2, difference Ar.

Lower graph: Feed composition: 475 ppmV of NO, difference Ar.

Temperature: 350°C, feed flow rate: 2 Nl min^{-1}. Experimental data: o, t_c = 60 s, □, t_c = 600 s; model predictions: solid lines.

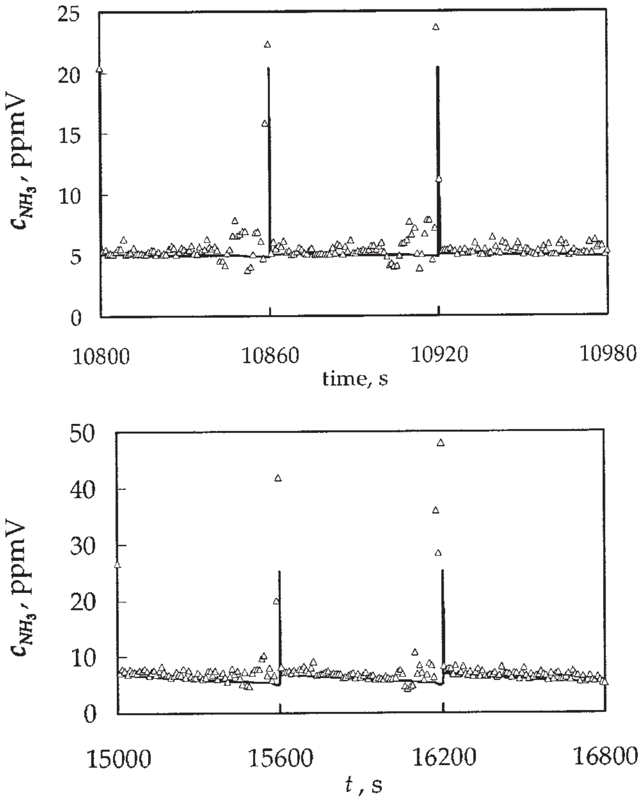

Figure 6. **Comparison between the model predictions (solid lines) and the experimental values (symbols) of the time evolution of the outlet NH_3 concentration during a period when the PSS has been reached.**

Feed composition: 485 ppmV of NH_3, 475 ppmV of NO, 1% O_2, difference Ar. Temperature: 350°C, feed flow rate: 2 Nl min^{-1}. Upper graph: t_c = 60 s, lower graph: t_c = 600 s.

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Notation

a_v = specific surface of the catalyst, m^{-1}
c = concentration
E_a = activation energy, J mol^{-1}
f = base line signal, A
h_i = mass transfer coefficient for the *i*th species, m s^{-1}
i_j = ionic current defined in Eq. A2
k = kinetic constant
k_0 = frequency factor
m = mass
N_c = number of cycles
q = electric charge
r = rate of reaction, mol s^{-1} m^{-3}
R = gas constant, J K^{-1} mol^{-1}
s_i = detected ionic current of fragment with mass *i*, A
t = time, s
t_c = switching time, s

T = temperature, K
x = axial coordinate, m
y_i = true signal generated by the molecule identified by the mass fragment *i*, A
v = gas velocity, m s^{-1}

Greek letters

$\alpha_{j,i}$ = interaction factor
β = parameter for the surface coverage dependence in Eq. 8
β_j = response factor of the QMS for the species *j*
θ = surface coverage
θ_B^ν = critical NH_3 surface coverage
σ = parameter for the surface coverage dependence in Eq. 8
Ω = catalyst capacity, mol m^{-3}

Subscripts and superscripts

0 = inlet condition
ads = adsorption
i, j = identify the species
des = desorption
red = reduction
A, B = reactants
S = solid phase
* = value at the gas-solid interface

Abbreviations

PSS = Periodic Steady State
QMS = Quadrupole Mass Spectrometer
RFR = Reverse-Flow Reactor
SCR = Selective Catalytic Reduction
SMB = Simulated Moving Bed

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Appendix

The working principle of a QMS is quite simple: a gas is sampled to the instrument and the molecules are fragmented, ionized, and accelerated by an electric field. The ions are characterized by a well defined value of mass (*m*) and electric charge (*q*), that is, by the ratio *m*/*q*. A filter separates the various ions depending on their *m*/*q* ratio: first, all the ions that do not have a unitary charge are eliminated from the current (this allows distinguishing the components of the mixture as a function of their molecular weight only); then the ions are driven to the detector, which gives a signal proportional to the concentration (and to the type) of the impacting fragment (each ion has its own proportionality constant). The resulting mass spectrum, constituted by the intensity of the current corresponding to each ion as a function of time, has to be manipulated to get the gas composition.

Each molecular species entering in the quadrupole chamber originates a wide variety of ions with different *m*/*q* ratio; as there is no chromatographic separation of the different species in the sample, ions with the same *m*/*q* may belong to different compounds. It is, therefore, necessary to select, for each species, the monitored ion avoiding, or at least minimizing, the interferences. Thus, in our application, the NH_3 has not been identified by the signal corresponding to the ions of mass 16 and 17 (which constitute the larger part of the spectrum of NH_3) as these ions belong also to O_2 and H_2O molecules, respectively, but the ion of mass 15 has been preferred. O_2 has been identified by the ion of mass 32 and NO by that of mass 30.

The signal corresponding to each ion is, in general, the sum of three different contributions, which are variable in time: the base signal, the interference signal, and the true signal. The base signal of a certain mass corresponds to the value of the ionic current when that mass is not present; this signal is not zero and changes in time are due to the intrinsic nature of the instrument and cannot be estimated a priori. Anyway, the base signal can be reasonably approximated with a linear function (see Figure A1). The calculus of the base line is done by imposing two points at the beginning and at the end of the run, that is, when the component starts to be fed and when the feeding is stopped:

$$f_j(t) = f_j^{(1)} + \frac{f_j^{(2)} - f_j^{(1)}}{t_2 - t_1} \cdot (t - t_1) \qquad \text{(A1)}$$

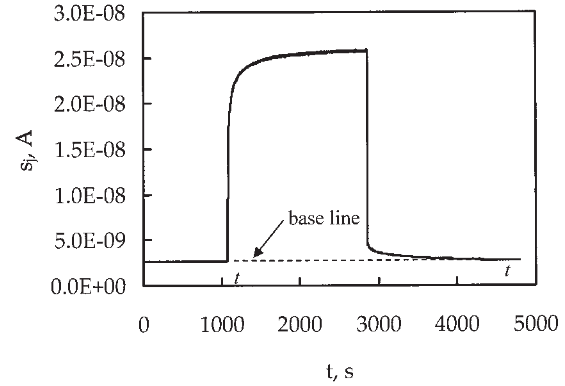

Figure A1. Time evolution of the ionic current of a mass j in a typical run.

where:

- $f_j(t)$ is the base signal for the mass j at time t;
- $f_j^{(1)}$ is the base signal for the mass j in the first point (time t_1);
- $f_j^{(2)}$ is the base signal for the mass j in the second point (time t_2).

The second contribution is a false signal generated by fragments of the species i that have the same m/q value of the fragment selected and monitored for the species j; this effect is named "interaction" and can be quantified:

$$i_j(t) = \sum_i (\alpha_{j,i} y_i(t)) \tag{A2}$$

where:

- $i_j(t)$ is the false signal;
- $\alpha_{j,i}$ is the proportionality constant;
- $y_i(t)$ is the signal of the fragment selected to monitor the interacting species i.

The interaction term $i_j(t)$ is obviously equal to zero if it is possible to identify the species j with an ion that is not originated by any other molecules.

The last contribution to the detected ionic current of mass j is the true signal generated by the molecule identified by the mass fragment, y_j. For the jth mass, it results:

$$s_j(t) = f_j(t) + i_j(t) + y_j(t) \tag{A3}$$

and thus:

$$y_j(t) = s_j(t) - f_j(t) - i_j(t) \tag{A4}$$

A linear dependence of concentration of the j species $c_j(t)$ from the signal $y_j(t)$ can be stated:

$$c_j(t) = \beta_j y_j(t) \tag{A5}$$

where β_j is the response factor of the instrument for the species j.

The calculation of the parameters $\alpha_{i,j}$ and β_j requires preliminary runs where the species j is introduced in the QMS and the variation of all the masses i is detected. It results:

$$\beta_j = \frac{c_j}{\Delta_{M,j}} \tag{A6}$$

where:

- c_j is the concentration of the species j in the feed;
- $\Delta_{M,j}$ is the variation of the ionic current of the mass fragment M selected to monitor the species j after the step introduction of this compound (in the absence of other interacting species); and

$$\alpha_{j,i} = \frac{\Delta_{M,i}}{\Delta_{N,i}} \tag{A7}$$

where:

- $\Delta_{M,i}$ is the variation of the ionic current of the selected mass fragment M after the step introduction of the compound i;
- $\Delta_{N,i}$ is the variation of the ionic current of the mass fragment N selected to monitor the interacting species i after the step introduction of this compound.

It is necessary to repeat the procedure described above before each run because the response factor of the instrument (and, thus, both $\alpha_{j,i}$ and β_j) is variable.

Let us consider, as an example, the application of this procedure to an experimental run for the calculation of the kinetic constant of the adsorption reaction of NH_3 over the catalyst. In this kind of experiment, a mixture of Ar, O_2, and NH_3 is fed to the reactor and the products, made up of Ar, O_2, and NH_3 not adsorbed, are sampled and analyzed in the QMS. For example, NH_3 gives rise to fragments of mass 17, 16, 15, while O_2 can originate fragments with mass 32, 16, 15, and so on. As has been stated before, mass 15 has been chosen to

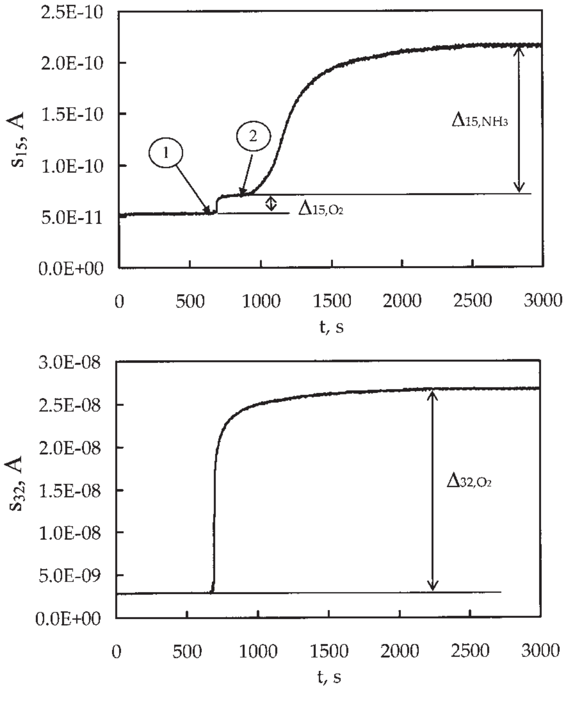

Figure A2. Time evolution of the ionic current of mass 15 and of mass 32 during an adsorption run.

identify NH_3 and mass 32 identifies O_2. As mass 15 is not the most abundant component of the spectrum of NH_3, the measured value is quite noisy. As a consequence, a standard FIR (Finite Impulse Response) filter algorithm available in the Filter Toolbox of MatLab has been used to filter the experimental values. The result, in terms of ionic current, is given in Figure A2 (point 1 identifies when the reactants have been introduced in the reactor). The ionic current corresponding to mass 32 is due to O_2; no other compounds can originate a fragment with this mass (the calculation of β_{o_2} is thus trivial); conversely, the ionic current corresponding to mass 15 is the result of the contribution of both O_2 and NH_3. At first only O_2 contributes to this signal as the NH_3 is adsorbed on the catalyst (up to point 2, in Figure A2), and this allows calculating α_{NH_3,O_2} by means of Eq. A.7. At the end of the experiment, when the ionic current of mass 15 does not exhibit any further changes, it can be assumed that all the catalyst is saturated and that the NH_3 concentration in the product stream is equal to that of the feeding. This allows calculating β_{NH_3}.

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