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SELECTIVE CATALYTIC REDUCTION OF NO_X WITH NH_3 IN UNSTEADY-STATE REACTORS

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ABSTRACT. The paper surveys the perspective of de-NO*x* Selective Catalytic Reduction (SCR) with ammonia in forced unsteady-state reactors. Two types of reactor configuration were investigated by means of numerical simulation: the well known reverse-flow reactor (RFR) and, as an alternative, a reactors network (RN) with periodical change of feeding position. While in the first device the unsteady-state operation results from periodical reversal of the flow direction, in the second one this is a consequence of modifying the reactor sequence in the network, the flow direction remaining the same; by this way ammonia emissions, which occur in RFR at every switch of flow direction and whose level is subject to stricter limits than for NO_x, is avoided. The influence of the switching time and of the switching strategy in the RN on the mean concentration of NH_3 and NO_x in the reactor outlet flow was also investigated.

Keywords: Reverse-flow reactor, Reactors Network, Chromatographic reactor, Selective Catalytic Reduction, Pollutant destruction

INTRODUCTION

Forced unsteady-state catalytic reactors have been a subject of intensive investigation by means of experiments and numerical simulations in the past several years. The unsteady-state operation may provide significant efficiency enhancement, increased selectivity, high productivity and low operating costs in a number of catalytic processes.

Unsteady-state operation may arise from variations (periodical or not) in the inlet flow rate, feed composition, temperature or pressure, as well as from the periodical reversal of the feed direction.

Reverse-flow operation has two main advantages: first, it allows for trapping the moving heat/concentration wave inside the catalytic bed when exothermic reactions take place, giving the possibility of exploiting the thermal storage capacity of the catalytic bed, which acts as a regenerative heat exchanger, allowing for auto-thermal behaviour even when the adiabatic temperature rise of the feed is low. Second, when exothermic equilibrium-limited reactions are carried out, the reversal of the flow allows for approaching the temperature distribution corresponding to maximum product generation. The Reverse-Flow Reactor (RFR) operation was suggested firstly by Cottrell (1938) as an efficient way to treat dilute pollutant mixtures.

The idea of using a RFR for destruction of a pollutant A with a reactant B, for which the maximum allowable emission is much lower than that of the first one, was firstly given by Agar and Ruppel (1988). They suggested to carry out the selective catalytic reduction (SCR) of NOx with ammonia in a RFR with a catalyst that strongly adsorbs the ammonia. This operation method is referred to as reverse flow chromatographic reactor (RFCR) and allows not only the trapping of the hot wave but also the trapping of ammonia in the bed minimizing its emissions and providing an effective response to reactant fluctuations in the feed rate.

Successful operation of a RFCR requires finding of a catalyst which strongly adsorbs the ammonia: the higher the adsorptivity, the more efficient is the operation.

Nevertheless the RFR exhibits the problem of wash out, i.e. the emission of unconverted reactants occurring when the flow direction is reversed.

The problem of wash out in the RFR was addressed by Brinkmann et al. (1999) in catalytic after-burners, by Velardi & Barresi (2002) in low pressure methanol synthesis and by Fissore, Barresi & Baldi (2003) in synthesis gas production. In all these papers an alternative reactor configuration was studied to avoid the occurrence of wash out, namely a Reactors Network (RN) made of two or three reactors connected in a closed sequence (Figure 1).

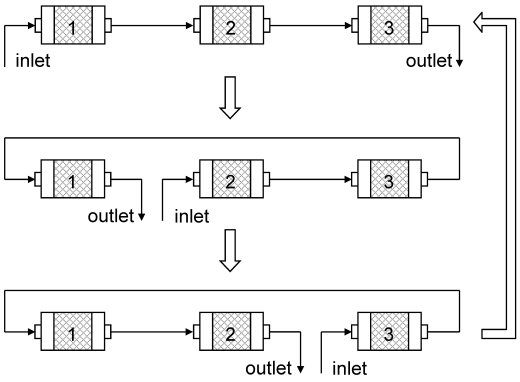

Figure 1. Exemple of Reactor Network operation

A set of valves enables to change the feed position, thus varying the sequence of reactors, simulating the behaviour of a moving bed, and achieving a sustained dynamic behaviour. Contrary to the RFR, the flow direction is maintained in this way, ensuring a uniform catalyst exploitation and avoiding wash out. One of the aim of this paper is thus to study the possibility of carrying out the SCR of NO_x with ammonia using the RN in order to overcome the problems aroused with the RFR.

The assumption of negligible temperature rise in the RFCR and isothermal condition is present in all the works concerning the SCR with NH_3. This allowed to simplify the analysis, enabling to focus on the impact of the operation strategy on the dynamic features caused by the trapping of one reactant in the reactor.

The adiabatic rise in NO_x removal is usually of the order of 10-20 K, but the temperature rise in a RFR can be a multiple of this value, thus allowing, for example, autothermal operation when low temperature gas is fed to the reactor. In this conditions, as it was stressed in the conclusion of the paper of Yong & Luss (2003), the choice of the switching time will be affected also by the dynamics of the heat wave, as too long switching time will lead to reaction extinction, due to the heat removal from the catalyst.

To study the possibility of improving the reactor operation we also have taken into account, beside the storage of the adsorbed ammonia on the catalyst bed, different chemical activities and adsorptive capacities of the catalyst.

The influence of reaction kinetics and catalyst characteristics will be stressed, as well as the influence of the switching time in both reactor configurations: this analysis is important not only as it allows to compare the two devices and to optimise the operation, but also as the switching time is the main operating parameter that can be changed to fulfil the operation constraints.

THE MODEL

An Eley-Rideal mechanism is used to describe the reaction between NO_x (A) in the gas phase and the ammonia (B) adsorbed on the catalyst:

$$A + B_S \rightarrow C\,; \tag{1}$$

$$B + S \rightarrow B_S\,. \tag{2}$$

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

$$r_{red} = -k_{red} c_{A,i} \theta_B\,; \tag{3}$$

where θ_B is the ammonia surface coverage and $c_{A,i}$ is the nondimensional concentration of reactant A at the gas-solid interface. 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 fraction of free surface sites:

$$r_{ads} = k_{ads} c_{B,i} \left(1 - \theta_B\right)\,; \tag{4}$$

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

$$r_{des} = k_{des} \theta_B\,. \tag{5}$$

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

$$\begin{aligned} k_{red} &= k_{0,red} e^{-\frac{E_{a,red}}{RT_S}} \\ k_{ads} &= k_{0,ads} e^{-\frac{E_{a,ads}}{RT_S}} \\ k_{des} &= k_{0,des} e^{-\frac{E_{a,des}}{RT_S}} \end{aligned}\,. \tag{6}$$

A Temkin-type adsorption isotherm, where the activation energy for desorption is a function of the surface coverage, is assumed:

$$E_{a,des} = E^0_{a,des}\left(1-\beta\theta_B{}^{\sigma}\right); \tag{7}$$

A surface coverage of this type was used in previous studies and was verified experimentally by Tronconi et al. (1996).

A monolith is considered for the SCR reaction. Solid catalytic surface is considered in pseudo-steady state conditions, pressure loss inside the reactor was neglected.

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

1. Gas phase mass balance:

$$\frac{\partial c_A^*}{\partial t^*} = -v^* \frac{\partial c_A^*}{\partial x^*} + Pe_A(c_{A,i}^* - c_A^*); \tag{8}$$

$$\frac{\partial c_B^*}{\partial t^*} = -v^* \frac{\partial c_B^*}{\partial x^*} + Pe_B(c_{B,i}^* - c_B^*); \tag{9}$$

where $C_A{}^*$ and $C_B{}^*$ are the non-dimensional gas concentration at the interface.

2. Solid phase mass balance:

$$\frac{\partial \theta_B}{\partial t^*} = Da_{ads} e^{-\gamma_{ads}\left(\frac{1}{T_S^*}-1\right)} c_{B,i}^*(1-\theta_B) - Da_{des} e^{-\gamma_{des}\left(\frac{1}{T_S^*}-1\right)} e^{\gamma_{des}\frac{\beta\theta_B^{\sigma}}{T_S^*}} \theta_B - Da_{red} e^{-\gamma_{red}\left(\frac{1}{T_S^*}-1\right)} c_{A,i}^* \theta_B \tag{10}$$

where:

$$x^* = \frac{x}{L},\ v^* = \frac{v}{v_0},\ t^* = t\frac{v_0}{L},\ c_A^* = \frac{c_A}{c_A^f},\ c_{A,i}^* = \frac{c_{A,i}}{c_A^f},\ c_B^* = \frac{c_B}{c_A^f},\ c_{B,i}^* = \frac{c_{B,i}}{c_A^f},\ Pe_A = \frac{h_A a_v L}{v_0},$$
$$Pe_B = \frac{h_B a_v L}{v_0},\ \gamma_{ads} = \frac{E_{a,ads}}{RT^f},\ \gamma_{des} = \frac{E^0{}_{a,des}}{RT^f},\ \gamma_{red} = \frac{E_{a,red}}{RT^f},\ Da_{ads} = \frac{k_{0,ads} e^{-\gamma_{ads}} L c_A^f}{v_0},$$
$$Da_{des} = \frac{k_{0,des} e^{-\gamma_{des}} L}{v_0}, \qquad Da = \frac{k_{0,red} e^{-\gamma_{red}} L c_A^f}{v_0} \tag{11}$$

Conventional Danckwerts boundary conditions are assumed at the inlet of the RFR and RN and the continuity of the gas concentration and temperature profiles are imposed between the reactors of the network.

Reactants are supposed to be feed at the same part of the reactor, inlet concentration of the gases are considered constant and equal to the feeding value, and the initial concentration of ammonia adsorbed on the catalyst surface is equal to zero in all the reactor configurations considered.

The system of Partial Differential Equations has been solved by discretizing the domain of spatial variable into a grid of 100 points, equally spaced, obtaining a grid-independent solution. The MatLAB solver ode15s was used to solve the system.

The influence of reaction kinetics and catalyst activity on NO_x selective catalytic reduction with ammonia in isothermal conditions system, both in the RFR and RN was investigated; process conditions used in sensitivity analysis are given in Table 1. Firstly, the values of *Da*, Da_{ads} and Da_{des} were varied, to point out the influence of kinetic activity and adsorption/desorption kinetic on the performance of the system. The results that can be obtained in the system with a commercial catalyst will be also shown: to this purpose the kinetic model proposed by Tronconi at al. (1996) for a V_2O_5/TiO_2 catalyst (with V_2O_5 loading of 1.47%) was used.

Table 1.

Values of the main operating parameters used in the simulations.

c_{NOx}	560 ppmV
c_{NH3}	450 ppmV
c_m	210 mol m^{-3}
L	0.45 m
v	0.27 m s^{-1}
a_v	200 m^{-1}

THE RESULTS

In order to investigate the influence of the unsteady-state operation mode on the adsorption-desorption of ammonia and on the reaction between ammonia and NO_x in the gas phase, the reactor was considered to operate in isothermal condition. Two different devices were considered, namely the RFR and a RN made of three reactors with variable position of the feed: the feeding position is moved from one reactor to the following one in the direct sequence, i.e. the system is fed through reactor number 1 and the order of the reactors is 1-2-3 and after a time period, the feed position is shifted, acting on a set of valves, so that the first reactor of the sequence becomes the third one, thus changing the order to 2-3-1.

When isothermal operation is assumed, as in this case, the switching time is the main operating parameter, particularly for control purposes. The influence of this parameter was investigated for different values of *Da* (Figure 2), of Da_{ads} (Figure 3) and of Da_{des} (Figure 4).

The inlet concentration of NO_x was fixed to 560 ppmV; a slightly lower concentration of ammonia (450 ppmV) was considered to be fed to the reactor.The performance of the devices were evaluated after the transient, when the periodic steady-state was reached, in terms of mean outlet concentrations of NO_x and of NH_3; the mean values were calculated over the entire length of a period.

The first evidence is that when either the catalyst activity or the adsorption kinetic are enhanced the emissions of both NO_x and NH_3 decrease, as it is expected; the same behaviour is obtained when the desorption kinetic is decreased. The influence of the switching time on the mean outlet concentration of NO_x and NH_3 in the RFR and in the RN is similar. At high switching time the performance of the RFR and that of the RN is the same both from the point of view of NO_x and NH_3 emissions. As far as lower values of the switching time are considered the emissions of NO_x and of NH_3 in the RFR are decreased when the switching time is increased as a consequence of the higher amount of ammonia which is stored in the catalyst. The performance of the RN is different: there is a first range of switching time where

the outlet ammonia concentration is almost zero and the outlet NO_x concentration decreases almost linearly; after this range, the outlet pollutant concentrations start increasing up to a certain value, before decreasing and approaching the behaviour of the RFR. This different behaviour can be explained considering the dynamics of the concentration profiles in the reactor: while in the RFR a bell shaped profiles is obtained as a consequence of the reversal of the flow direction, in the RN more complex profiles may be obtained and, as a consequence of the switching strategy, the ammonia profile may exit from one of the reactors of the network, thus giving rise to higher reactants emissions. This behaviour is similar to that observed for the temperature profile in the RN by Brinkmann et al. (1999).

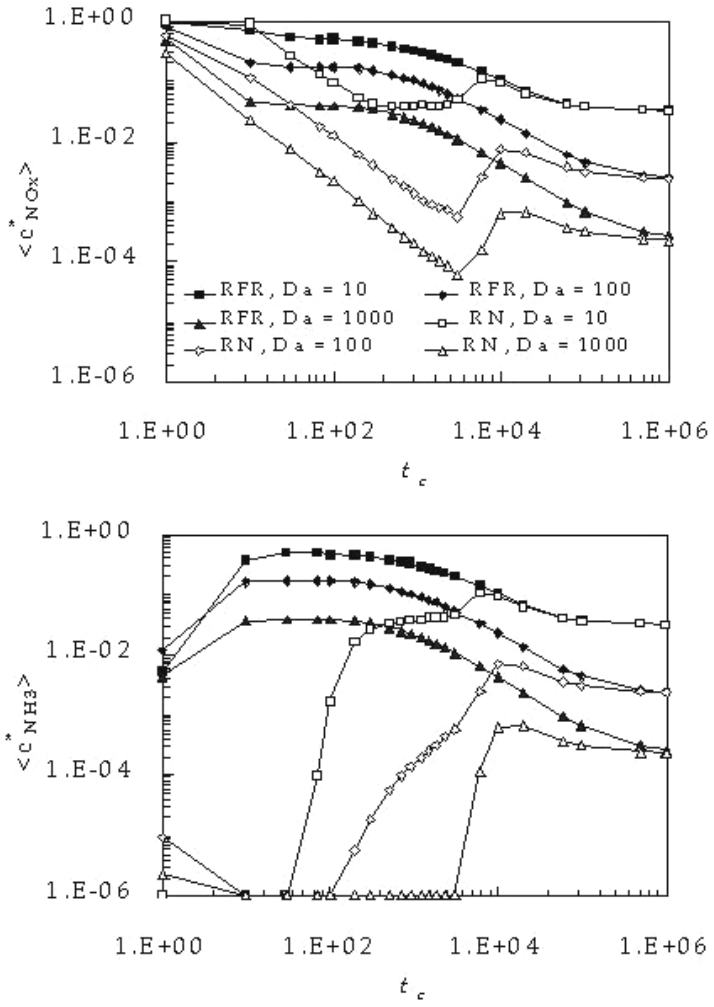

Figure 2. Influence of the switching time on the mean outlet non-dimensional concentration of NO_x (upper graph) and of ammonia (lower graph) for various values of *Da* in the RFR and in the RN (isothermal system).

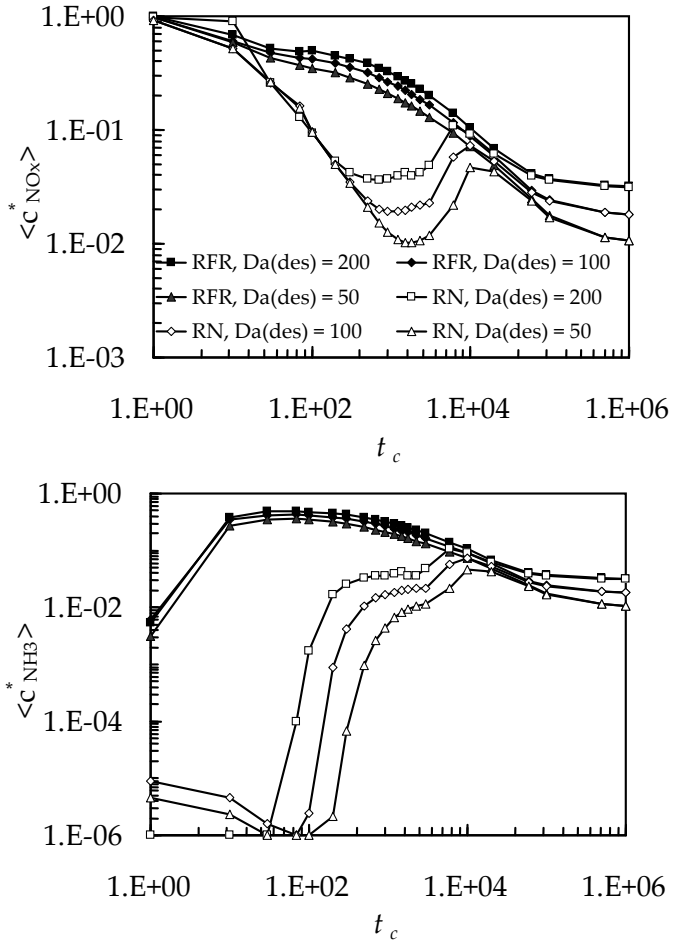

Figure 3. Influence of the switching time on the mean outlet non-dimensional concentration of NO_x (upper graph) and of ammonia (lower graph) for various values of $Da_{(des)}$ in the RFR and in the RN (isothermal system).

In conclusion, there is a wide range of switching time where the RN exhibits no ammonia emissions and NO_x emissions lower than those obtainable in the RFR; this is a consequence of the absence of wash out, as discussed previously; the extent of this "optimal" range is a function of the parameter of the system, namely Da, Da_{ads}, Da_{des}.

Finally, the performance obtainable with a commercially available catalyst are considered. In this case several different design configurations are investigated. The kinetic model of Tronconi et al. (1996) was used for the simulations. The influence of the switching time was analysed in various configurations, namely the RFR and the RN made up of two and three reactors (with different switching strategy). The

influence of the switching time on the mean outlet concentration of NO_x and NH_3 is very different from that previously obtained: a maximum value of switching time is found beyond which conversion decreases both in the RFR and in the RN. As far as the ammonia outlet concentration is concerned, the value decreases when the switching time is increased in the RFR, while in the various RN considered a minimum appears. It is important to notice that it is mandatory that no ammonia is present in the product stream, thus only the three reactors network with switching strategy 1-2-3 -> 3-1-2 can be used, even if this results is achieved in a narrow range of switching times. On the contrary, the RFR can be operated with switching time between 600 and 3000 in order to avoid NO_x emissions, even if a certain amount of NH_3 is released from the reactor.

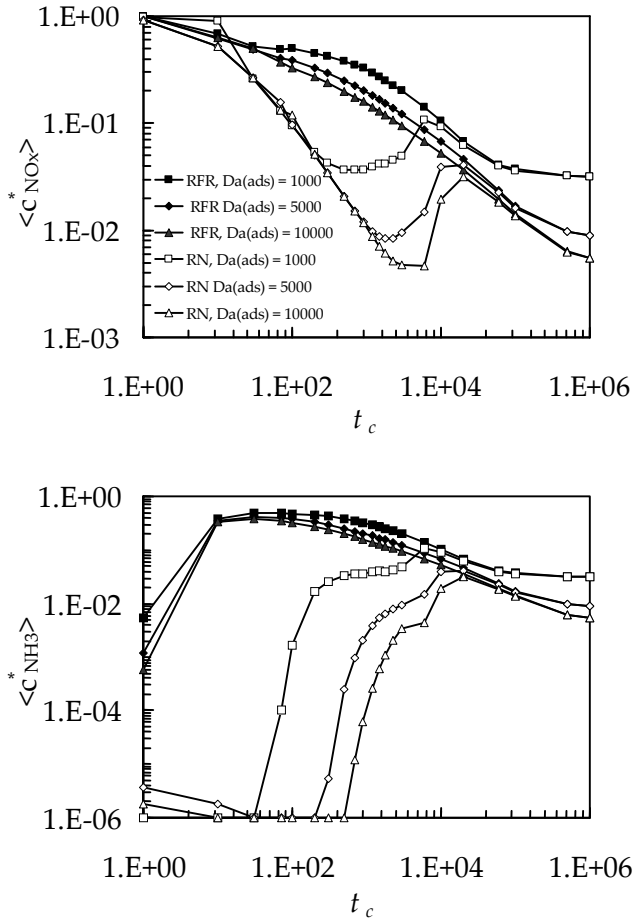

Figure 4. Influence of the switching time on the mean outlet non-dimensional concentration of NO_x (upper graph) and of ammonia (lower graph) for various values of $Da_{(ads)}$ in the RFR and in the RN (isothermal system).

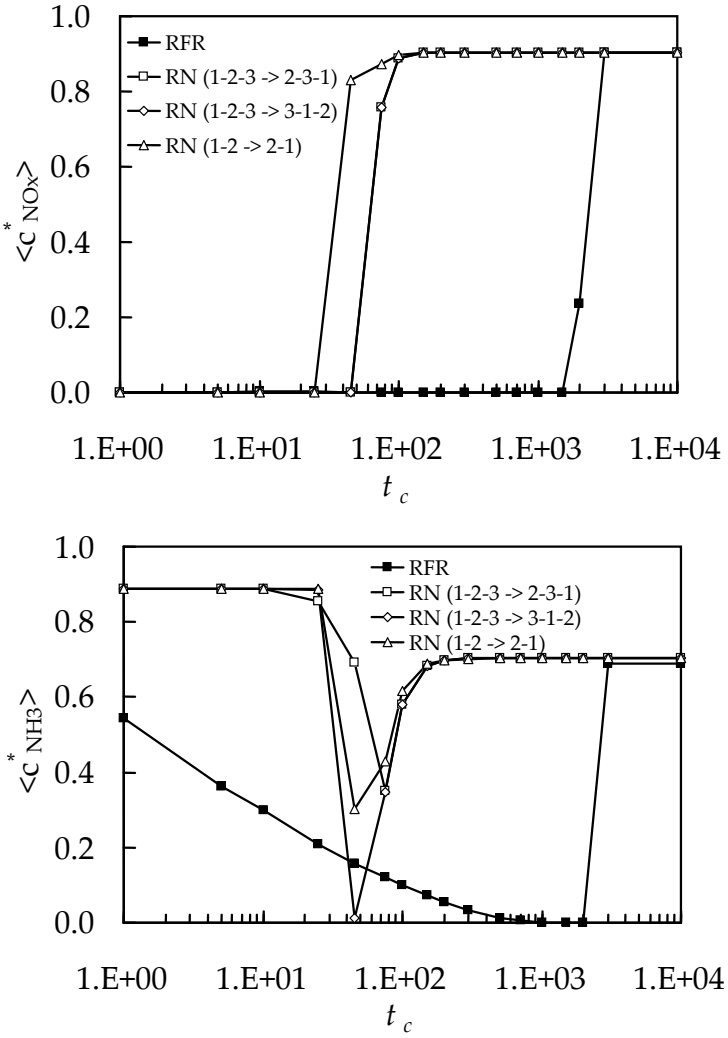

Figure 5. Influence of the switching time on the mean outlet non-dimensional concentration of NO_x (upper graph) and of ammonia (lower graph) in the RFR and in various configurations of the RN for the operating parameters of Table 1 (isothermal system).

This behaviour, which is different from that shown in Figures 2-4, can be explained if the values of *Da*, $Da_{(ads)}$, $Da_{(des)}$ are calculated for the commercial catalyst considered in the paper of Tronconi et al. (1996): for example *Da* is very high, about 10^5, thus altering the dynamic of the system in comparison to the values previously considered and masking the wash out phenomena.

CONCLUSIONS

The feasibility of SCR of NO_x with ammonia in unsteady-state reactors was studied for various reactors configurations by means of numerical simulations, using a heterogeneous mathematical model and an Eley-Rideal kinetic mechanism. Isothermal system, in which the problem of the heat storage in the system is neglected, was simulated. The results are strongly influenced by the system parameter, namely *Da* (kinetic constant of the reduction reaction), $Da_{(ads)}$ (kinetic constant of the adsorption reaction) and $Da_{(des)}$ (kinetic constant of the desorption reaction). In particular, when the adsorption and the reaction rate are not very high, the RN, which does not exhibits the wash out phenomena, is the only device which ensures the fulfilment on the emissions limits for the two reactants, while when the adsorption and the reaction rate are very high, as in the case of the system of Tronconi et al. (1996), the results are different, and the RFR has to be preferred as the problem of wash out is bypassed by the high adsorption and reaction rate.

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NOTATION

C^*	non-dimensional concentration
c	concentration, mol m^{-3}
c_A^f	concentration of reactant A in the feed, mol m^{-3}
Da	Damkohler number
E_a	activation energy, J mol^{-1}
h_A, h_B	mass transfer coefficients
k	reduction kinetic constant, m^3 mol^{-1} s^{-1}
k_0	pre-exponential factor of the reduction kinetic constant, m^3 mol^{-1} s^{-1}
k_{ads}	adsorption kinetic constant, m^3 mol^{-1} s^{-1}
$k_{0,ads}$	pre-exponential factor of the adsorption kinetic constant, m^3 mol^{-1} s^{-1}
k_{des}	desorption kinetic constant, s^{-1}
$k_{0,des}$	pre-exponential factor of the desorption kinetic constant, s^{-1}
L	total reactor length, m
Pe	Peclet number for mass transport
R	ideal gas constant, J mol^{-1} K^{-1}
r	reaction rate, mol m^{-3} s^{-1}
T	temperature, K
t	temporal coordinate, s
t^*	non-dimensional temporal coordinate
t_c	non-dimensional switching time
T^f	inlet gas temperature, K
v	gas velocity, m s^{-1}
v_0	superficial velocity

v^*	non-dimensional gas velocity
x	axial coordinate, m
x^*	non-dimensional spatial coordinate

Greeks

β	parameter for surface coverage dependence
γ	non-dimensional activation energy
θ	surface coverage
σ	parameter for the surface coverage dependence

Subscripts and superscripts

ads	adsorption process
A	identifies NO_X
B	identifies NH_3
B_S	identifies NH_3 adsorbed
des	desorption process
i	interface
S	solid

Abbreviations

RFCR	Reverse-flow Chromatographic Reactor
RF	Reverse-flow Reactor
RN	Reactors Network
SCR	Selective Catalytic Reduction

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