Ammonia Selective Catalytic Reduction of NO in a Monolithic Reverse Flow Reactor

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Nitrogen oxides (NO_x) contribute to the greenhouse effect (besides CO_2, CH_4 and H_2O) and take part in photochemical reactions that lead to smog and acid rain formation. That is way their removal from emissions to the atmosphere is one of the most important environmental problems nowadays. One of the most efficient techniques for NO_x abatement is the selective catalytic reduction of NO_x by NH_3 (NH_3-SCR). In this study the performance of reverse flow reactors (RFR, a fixed bed reactor in which the direction of the inlet flows is reversed periodically), is evaluated for NO_x removal. Therefore, a mathematical model was developed in order to determine the optimal SCR operation conditions.

1. Introduction

1.1 NO_x abatement

The concentration of anthropogenic pollutants in the atmosphere has increased rapidly throughout the last decades. This increase is due, basically, to the combustion of fossil fuels and biomass. Nitrogen oxides (NO_x) is a group of air pollutants, including nitrogen oxide, nitrogen dioxide and nitrous oxide, considered as very dangerous, as they contribute to the greenhouse effect and participate in photochemical reactions that lead to acid rain and tropospheric ozone.

The three major techniques for NO_x abatement are lean NO_x traps (LNT), ammonia- or urea- Selective Catalytic Reduction (NH_3-SCR) and Hydrocarbons Selective Catalytic Reduction (HC-SCR) (Lietti et al., 2008; Galvez et al., 2006).

NH_3-SCR has been used mainly for stationary sources, due to its high efficiency and the ability of ammonia to react selectively with NO_x forming N_2, together with the resistance to poisoning and aging of the catalysts used.

NH_3-SCR is based on the reaction between NO_x and NH_3 to produce water and nitrogen, according to the following reactions:

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O \tag{1}$$

$$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O \tag{2}$$

$$8\ NH_3 + 6\ NO_2 \rightarrow 7\ N_2 + 12\ H_2O \tag{3}$$

Since NO_x typically consist of >90% NO, the first one is largely the most important.

Many different catalysts have been studied for NH_3-SCR, such as WO_3-V_2O_5 and MoO_3-V_2O_5 supported on TiO_2, other transition metal oxides such as Mn/TiO_2,

Cu/TiO$_2$, Cr/TiO$_2$ and Fe/TiO$_2$ and zeolites (Alemany et al., 1995; Li et al., 2007; Busca et al., 1998).

SCR catalysts are generally used as structured beds. Structured beds produce lower pressure drop through the reactor than particulate beds. Furthermore, structured catalysts help to keep process conditions uniform along the bed and present higher resistance to attrition and lower tendency to fly ash plugging. Depending on the concentration of dust, plate-type or honeycomb structures are selected.

1.2 NH$_3$-SCR reactors

The most common reactor used for NH$_3$-SCR is the fixed bed reactor, either with particulate or structured catalyst (Irfan et al., 2008). Fluidized beds (Tran et al., 2008), and reactors operating in forced unsteady state, such as loop reactors and reverse flow reactors (Noskov et al., 1993) have also been studied.

RFR consist of a fixed bed catalytic reactor in which the direction of the feed flow is reversed periodically. RFR configuration presents several potential advantages (Fissore et al., 2006) as stable autothermal operation even for very slightly exothermic reactions (Matros and Bunimovich 1996). RFR have been investigated for different applications, including the treatment of lean air-hydrocarbon mixtures, the oxidation of SO$_2$ and the reduction of NO$_x$ emissions (Pinoy and Hosten 1993). Regarding the application to NH$_3$-SCR, RFR allow the decrease of un-reacted NH$_3$ emissions, as ammonia is trapped in the exit section of the bed. Thus, NH$_3$ leaks and inlet NO fluctuations are easier to control.

In this work, the performance of RFR is evaluated for NO$_x$ removal by simulations in order to determine the optimal operation conditions.

2. Methodology

2.1 Kinetic model

Several reaction mechanisms and kinetic models have been proposed for ammonia-SCR (Odenbrand et al., 1994). In this work, a mechanism in which NO reacts with ammonia, previously adsorbed on the catalyst surface has been used (Tronconi et al., 1996).

The SCR adsorption/desorption and reduction parameters can be determined by the transient response method, measuring the reactants concentration profile *vs.* time. Assuming isothermal plug flow and negligible mass transfer resistances, the kinetic model and mass balances for the gas phase and for the catalyst surface can be simplified. The resulting equations are listed below:

NH$_3$ adsorption, desorption and reduction respectively

$$r_{ads}=k_{ads}\ c_{NH_3,i}\left(1-\theta_{NH_3}\right)\Omega\ ; \quad k_{ads}=k_{0,ads}\ e^{-E_{a,ads}/R\cdot T_s} \tag{4}$$

$$r_{des}=k_{des}\ \theta_{NH_3}\Omega\ ; \quad k_{des}=k_{0,des}\ e^{-E_{a,des}/R\cdot T_s}\ ; \quad E_{a,des}=E_{a0,des}\left(1-\beta\cdot\theta_{NH_3}^{\sigma}\right) \tag{5}$$

$$r_{red}=k_{red}\ c_{NO,i}\ \theta_{NH_3}\ \Omega\ ; \quad k_{red}=k_{0,red}\ e^{-E_{a,red}/R\cdot T_s} \tag{6}$$

Gas and solid phase mass balance

$$\frac{dC_{NO}}{dt} = -v\frac{dC_{NO}}{dz} - r_{red} \; ; \qquad \frac{dC_{NH_3}}{dt} = -v\frac{dC_{NH_3}}{dt} + r_{ads} - r_{des} \qquad (7)$$

$$\Omega \frac{d\theta_{NH_3}}{dt} = r_{ads} - r_{des} - r_{red} \qquad (8)$$

The model uses Temkin isotherm as it was found that it fits the experimental data better than the Langmuir isotherm; activation energy for NH_3 adsorption is taken as zero.

2.2 RFR model

The model for RFR considered in this work is non-stationary mono-dimensional heterogeneous. A one-dimension model was chosen balancing model accuracy and complexity, as it offers reasonable accuracy, with moderate complexity. Regarding the phases involved, a heterogeneous model has been chosen, as it allows evaluation of the solid and gas properties separately.

The resulting mathematical model consists of a system of partial differential-algebraic equations. The differential equations are obtained from conservation equations, both to the solid and the gas phases, while the algebraic equations correspond to the estimation of physical and transport properties. The model considers both internal and external mass and heat transfer resistances, as well as axial dispersion. The main equations for the RFR model, as well as a thoughtful study of its application for methane combustion can be found in (Marin et al., 2005).

2.3 Experimental apparatus

The parameters needed for the mathematical simulations have been determined using two experimental devices. The catalyst adsorption parameters and the reaction kinetics where studied in a fixed bed reactor (a 7 mm i.d. and 14 cm length stainless steel cylinder, filled with 0.5 g of catalyst, grinded to 250-355 mm, in order to limit mass transfer effects). Mass transfer coefficients were studied in a RFR unit consisting of two twin sections, 6 cm diameter and 50 cm length stainless steel cylinder each, filled with a commercial monolithic catalyst. In both units the reactors were thermally controlled so that they could operate in isothermal conditions. Mass flow controllers regulated feed flow rates, and, in the RFR unit, a system of solenoid valves allowed the periodic flow reversal. Chemical analysis was performed on line by mass spectrometry.
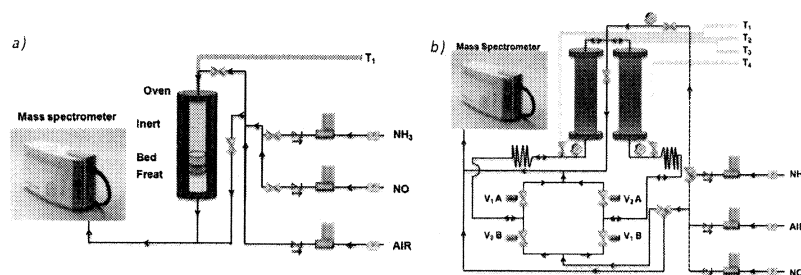

Figure 1: Scheme of the experimental devices for a) kinetics and adsorption parameters and for b) Mass transfer coefficient estimation.

3. Results and discussion

3.1 Kinetics and adsorption parameters

The values of the adsorption desorption and reduction parameters were obtained in the small fixed bed reactor by applying the transient response method as described in (Berger et al., 2008). The fitted parameters are shown in Table 1. Experiments were carried out at three temperatures, varying the feed flow rate and NO concentration, and the NH_3/NO inlet ratio. Ammonia oxidation was also studied at different O_2 concentrations.

Table 1: Fitted kinetic parameters values

Parameter	Units []	Value
Ω (capacity of the catalyst)	mol NH_3 kg cat^{-1}	0.19
k_{ads}	s^{-1}	2.90
k_{des}	s^{-1}	$5.16 \; 10^{-2}$
$E_{a, des}$	J mol^{-1}	$4.83 \; 10^{4}$
β (Temkin isotherm parameter)		0.77
k_{red}	m^{3} mol^{-1} s^{-1}	$5.72 \; 10^{8}$
$E_{a, red}$	J mol^{-1}	$1.44 \; 10^{5}$

3.2 Mass transfer coefficients optimization

Some reactor parameters, such as bed porosity, catalyst tortuosity and thickness of the wash-coating layer were optimized trough experiments in the RFR unit operating as a regular fixed bed reactor (with no switching of the flow direction). As an example, Figure 2 shows the influence of the bed porosity on the predicted ammonia concentration vs. time for a specific adsorption experiment conditions (Q = 12LN·min^{-1} and T = 185°C).

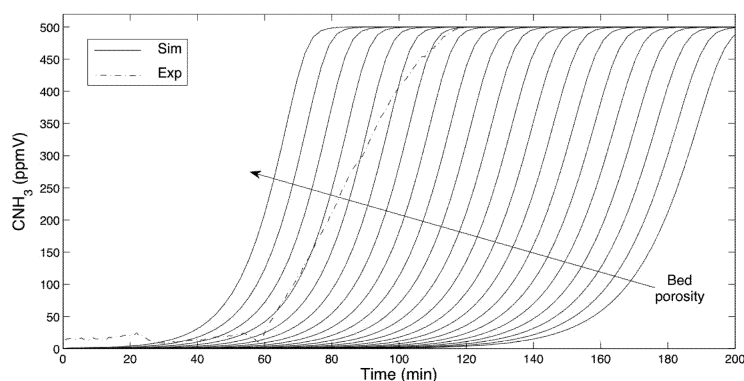*Figure 2: Influence of bed porosity testing the adsorption of NH₃. Dashed line corresponds to experimental values, while solid lines correspond to simulation results.*

3.3 RFR simulations

Once the values of the parameters needed to solve the RFR model are available, the effect of the main variables that affect the RFR operation on the system performance and stability can be studied. Within the variables studied, the most relevant are feed flow rate, feed composition (NO concentration and NH_3/NO ratio), inlet feed temperature, reactor length and switching time.

Figs. 3 and 4 show a sample of the results obtained, i.e. the evolution of ammonia adsorpted and outlet NO concentration with temperature respectively.
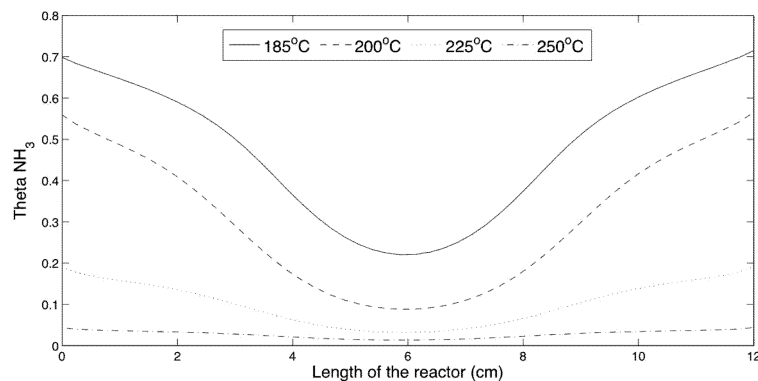

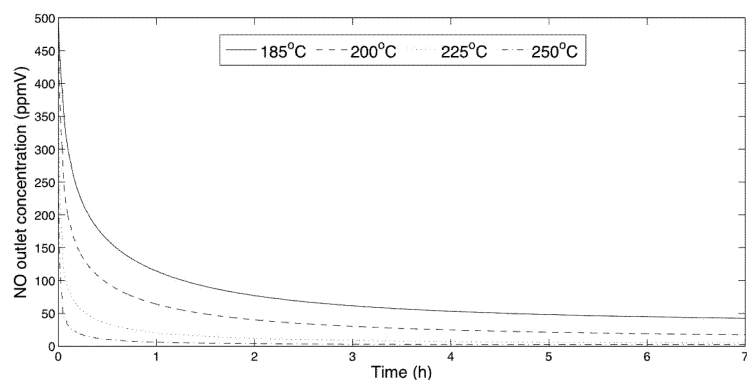*Figure 3: Evolution of ammonia adsorpted onto the catalyst at different temperatures.*

Figure 4: Evolution of outlet NO concentration at different temperatures.

Results show that for the conditions considered, operating below 200°C lead to lower NO conversion, and to higher amount of ammonia adsorpted on the catalyst.

4. Conclusions

The method used to determine the values of the parameters needed to simulate the RFR operation as shown to be adequate, and the resulting model is very useful for studying the influence of the operating conditions on the RFR performance for NH_3-SCR. Thus,

some variables such as the fraction of ammonia adsorpted onto the catalyst can be evaluated and related to the external variables that are easier to monitor. Besides this, some conditions that are difficult or risky to study (i.e. inlet temperature unusually high) can be studied by simulations.

References

Alemany L.J., Lietti L., Ferlazzo N., Forzatti P., Busca G., Giamello E. and Bregani F., 1995, Reactivity and physicochemical characterization of V_2O_5-WO_3/TIO_2 De-NO_x catalysts. Journal of Catalysis, 155 (1), 117-130.

Berger R., Kapteijn F., Moulijn J., Marin G., De Wilde J., Olea M., Chen D., Holmen A., Lietti L., Tronconi E. and Schuurman Y., 2008, Dynamic methods for catalytic kinetics. Applied Catalysis A: General, 342 (1-2), 3-28.

Fissore D., Barresi A.A. and Botar-Jid C.C., 2006, NO_x removal in forced unsteady-state chromatographic reactors. Chemical Engineering Science 61 (10), 3409-3414.

Galvez M. E., Boyano A., Lazaro M. J. and Moliner R., 2008, A study of the mechanisms of NO reduction over vanadium loaded activated carbon catalysts. Chemical Engineering Journal, 144 (1), 10-20.

Irfan M.F., Goo J.H. and Kim S.D., 2008, Co_3O_4 based catalysts for NO oxidation and NO, reduction in fast SCR process. Applied Catalysis B: Environmental, 78 (3-4), 267-274.

Li L., Zhang F., Guan N., Richter M., and Fricke R., 2007, Selective catalytic reduction of NO by propane in excess oxygen over IrCu-ZSM-5. Catalysis Communications, 8 (3), 583-588.

Lietti L., Nova I. and Forzatti P., 2008, Role of ammonia in the reduction by hydrogen of NO_x stored over Pt-Ba/Al_2O_3 lean NO_x trap catalysts. Journal of Catalysis, 257 (2), 270-282.

Marín P., Hevia M.A.G., Ordoñez S. and Díez F.V., 2005, Combustion of methane lean mixtures in reverse flow reactors: Comparison between packed and structured catalyst beds. Catalysis Today, 105 (3-4), 701-708.

Matros Y.S. and Bunimovich G.A., 1996, Reverse-flow operation in fixed bed catalytic reactors. Catalysis Reviews, 38: 1-68.

Noskov A.S., Bobrova L.N. and Matros Y.S., 1993, Reverse-process for NO_x-off gases decontamination. Catalysis Today, 17 (1-2), 293-300.

Odenbrand C., Bahamonde A., Avila P. and Blanco J., 1994, Kinetic-study of the selective reduction of nitric-oxide over vanadia-tungsta-titania sepiolite catalyst. Applied Catalysis B: Environmental, 5 (1-2), 117-131.

Pinoy L.J. and Hosten L.H., 1993, Experimental and Kinetic Modelling study of DeNO$_x$ on an Industrial V_2O_5-WO_3/TiO_2 catalyst. Catalysis Today, 17 (1-2), 151-158.

Tran K.Q., Kilpinen P. and Kumar N., 2008, In-situ catalytic abatement of NO_x during fluidized bed combustion - A literature study. Applied Catalysis B: Environmental, 78 (1-2), 129-138.

Tronconi E., Lietti L., Forzatti P. and Malloggi S., 1996, Experimental and theoretical investigation of the dynamics of the SCR-DeNOx reaction. Chemical Engineering Science, 51 (11), 2965-2970.