A new generation of Rhône-Poulenc DeNOx catalyst: DN115

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Anticipating more stringent emission limits, Rhône-Poulenc has developed a new generation of selective catalytic reduction (SCR) catalyst named DN115 improving performances especially at low temperature. Data on the commercially available vanadium oxide-based catalyst DN115 are presented. Effects of operating temperature, pressure, gas composition and space velocity are also investigated. A kinetic model has been established. The DN115 catalyst is also effective for the control of a variety of other NOx emissions, such as industrial boilers like chemical waste incineration or other chemical processes.

Keywords: NOx selective reduction; vanadium oxides; kinetic model

1. Introduction

Nowadays, more than ever, environmental problems have become a reality and a major priority. Approximately 600 million tons of nitrogen oxides are emitted into the atmosphere every year [1]. It is well known that nitrogen oxides contribute to the formation of smog, acid rain and ozone [2–4]. The two man-made sources of NOx come from motor vehicles [5] for one-half and the other half from oil and coal-fired power stations, industrial ovens and chemical processes [6]. Among this last, chemical processes such as production of nitric acid have received a lot of attention due to their high concentration and, in many cases, their locations near large urban populations.

Rhône-Poulenc is a major nitric acid producer and user. Therefore, for the last fifteen years or so, it has undertaken intensive studies on the reduction of NOx emission from nitric acid plants [7–9]. Today, the selective catalytic reduction (SCR) catalyst system has been recognized as the most powerful process for NOx reduction, with more than 400 reactors installed all over the world and more particularly in Asia and in Europe.

Our recent research has been targeted at improving the performances of our catalyst at low temperature. This was achieved using a new generation of DeNOx catalyst named DN115. A summary of the performances under typical nitric acid plant tail gas conditions is presented in this paper.

2. Experimental

The Rhône-Poulenc DeNOx catalyst DN115 consists of γ-alumina spheres (3 mm diameter) on which 13 wt% vanadium pentoxide is deposited. The pore structure as well as the surface area of the alumina carrier was optimized to allow efficient diffusion of NOx and NH_3, increasing the catalytic performances without sacrificing the mechanical strength [10]. Careful control of the impregnation procedure leads to a high dispersion of the vanadium oxide on the alumina.

The catalyst was evaluated for NOx removal activity in an automated bench scale pilot unit with a fixed-bed integral flow reactor described previously [7].

3. Results and discussion

Effects of the main process variables on the performances of the DN115 catalyst are reviewed.

3.1. *Effect of temperature*

The temperature dependence of the catalytic activity of the DN115 catalyst for the NOx reduction is shown in fig. 1 considering the typical industrial conditions of a nitric acid plant and for an ammonia slip lower than 1 vpm. The result indicates that a temperature as low as 170°C gives a NOx conversion, defined as

$$\text{NOx conversion } \% = 100(\text{NOx inlet } - \text{NOx outlet})/\text{NOx inlet}\,,$$

higher than 95%. This value shows clearly the high efficiency of the catalyst at low temperature. Fig. 2 shows the improvement of NOx removal performances of DN115 versus the previous Rhône-Poulenc catalyst DN110 at low temperature.

Above 400°C, the oxidation of ammonia to nitrogen and nitrous oxide according to the equations

$$4NH_3 + O_2 \rightarrow 2N_2 + 6H_2O \quad (1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (2)$$

compete with the reduction of NOx and leads to a

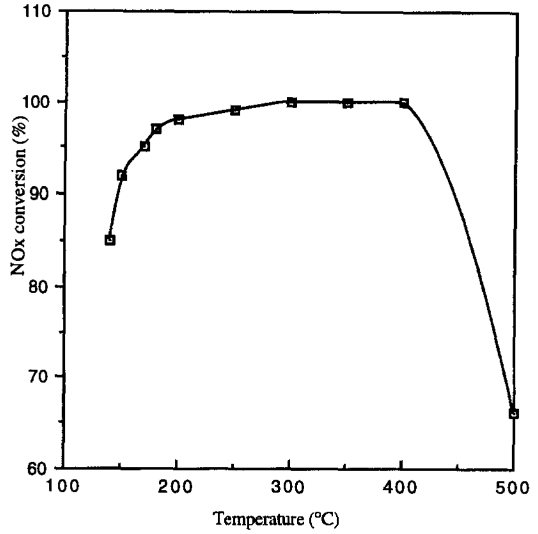

Fig. 1. NOx conversion versus temperature for DN115; pressure = 4 bar abs.; space velocity = 8000 h^{-1}; NO_2 = 800 vpm; NO = 1200 vpm; O_2 = 3%; NH_3 slip < 1 vpm.

decrease in NOx conversion at constant inlet NH_3/NOx molar ratio. Nitrous oxide becomes significant only above 400°C. However, the levels of N_2O formed over the DN115 catalyst are negligible (lower than 20 vpm measured) in the typical temperature range for nitric acid plant tail gases.

3.2. Effect of pressure

The pressure dependence of the catalytic activity of DN115 is presented in fig. 3 at pressures of 1–7 bar absolute at low temperature 170°C. The positive effect on the NOx conversion of the total gas pressure observed may be explained by an enhancement of NO adsorption on reduced vanadium sites.

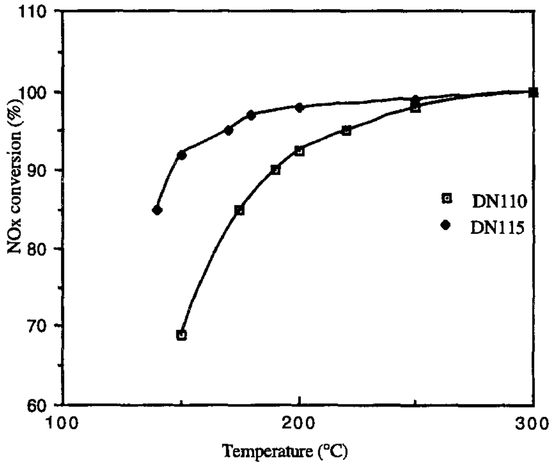

Fig. 2. Effect of temperature on NOx conversion for DN110 and DN115; pressure = 4 bar abs.; space velocity = 8000 h^{-1}; NO_2 = 800 vpm; NO = 1200 vpm; O_2 = 3%; NH_3 slip < 1 vpm.

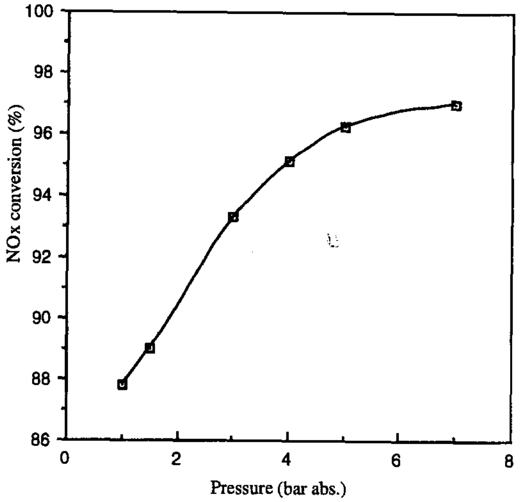

Fig. 3. NOx conversion versus pressure for DN115; temperature = 170°C; space velocity = 8000 h^{-1}; NO_2 = 800 vpm; NO = 1200 vpm; O_2 = 3%; NH_3 slip < 1 vpm.

3.3. Effect of time contact

Fig. 4 presents the NOx conversion over DN115 at 170°C versus time contact defined as the opposite of space velocity. It is important to notice the high NOx conversion observed over a large range of time contact 0.1–0.7 s.

3.4. Effect of gas composition

In fig. 5 are presented NOx conversion versus NOx composition or oxidation ratio defined as the inlet ratio of NO_2 in the NO + NO_2 mixture. The NOx reduction at equimolar composition proceeds at much higher rate than both NO and NO_2 reduction. This result can be due to a higher rate of formation of N_2O_3(ads) intermediate

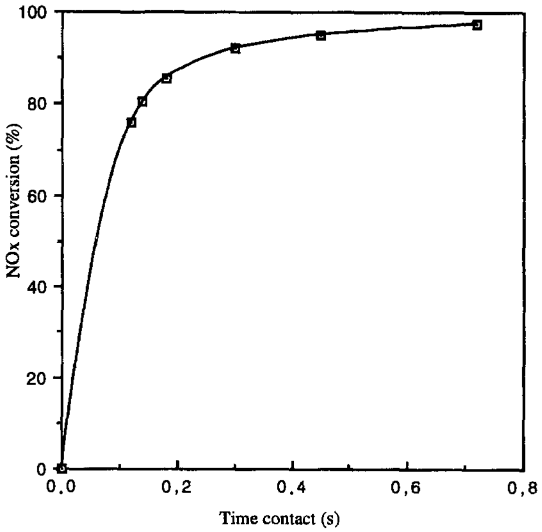

Fig. 4. NOx conversion versus time contact for DN115; temperature = 170°C; pressure = 4 bar abs.; NO_2 = 800 vpm; NO = 1200 vpm; O_2 = 3%; NH_3 slip < 1 vpm.

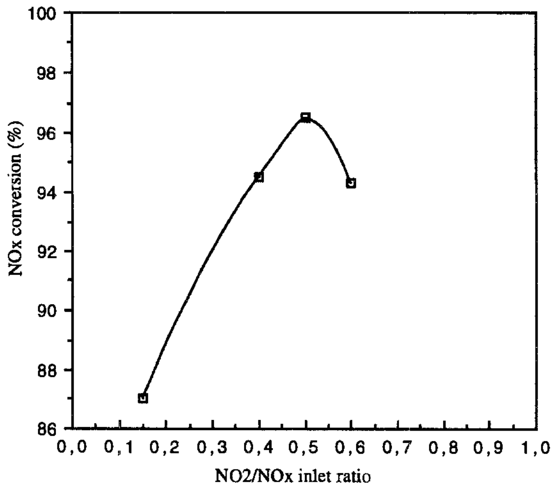

Fig. 5. NOx conversion versus gas composition for DN115; temperature = 170°C; pressure = 4 bar abs.; NOx = 2000 vpm; O_2 = 3%; space velocity = 8000 h^{-1}; NH_3 slip < 1 vpm.

species proposed in the Langmuir–Hinshelwood mechanism for the reduction of NOx by ammonia [7] and confirmed by mass spectrometry [11].

Nitrous oxide was detected at the outlet of the catalyst only when the proportion of NO_2 in NOx was greater than 70%. However, the amounts observed were lower than 70 vpm in the conditions considered. The formation of N_2O at temperatures below the onset of ammonia oxidation (350°C) follows the overall reaction [9]

$$8NO_2 + 10NH_3 \rightarrow 8N_2 + N_2O + 15H_2O \qquad \Delta G^{\circ}_{443} = -3678 \text{ kJ/mol} \tag{3}$$

and becomes significant only in the presence of a large excess of NO_2 with respect to NO.

3.5. Kinetic model

From the activity test results, we observed a significant deviation from the pseudo-first-order kinetics found by other investigators [12] and we confirm that the best fit corresponds to an order of 3/2 according to eq. (4) as we have seen previously with the DN110 catalyst [7],

$$[1/(1-X)^{n-1}] - 1 = (n-1)KT_c\,. \tag{4}$$

The value of n is 3/2 in the temperature range of 140–350°C, where X is the NOx conversion and T_c is the contact time.

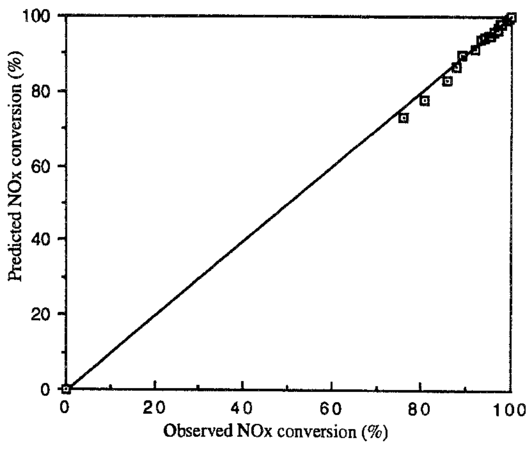

Fig. 6. Comparison of predicted and observed NOx conversion for DN115.

Taking into account the effects of the main process variables seen previously on the performances of the DN115 catalyst, we can deduce the global empirical rate expression:

$$X = 1 - 1/[1 + K\mathrm{e}^{-4142/T}(P_a T_c)]^2\,, \tag{5}$$

where X is the NOx conversion, T is the temperature (K), P is the total pressure (bar) and T_c is the contact time (s). In fig. 6 are shown the calculated conversions obtained from eq. (5) versus experimental values. It is clear that eq. (5) fits very well all experimental data over the entire range of conditions considered.

References

[1] J. Roiron, Nitrogen 86, Amsterdam, April 1986.
[2] F. Luck and J. Roiron, Catal. Today 4 (1989) 205.
[3] H. Bosch and F. Janssen, Catal. Today 2 (1988) 369.
[4] Z.R. Ismagilov, M.A. Kerhentsev and T.L. Susharina, Russ. Chem. Rev. 59 (1990) 973.
[5] G.J.K. Acres, in: *Perspectives in Catalysis*, eds. J.M. Thomas and K.I. Zamaraev (Blackwell, IUPAC, 1992) p. 359.
[6] H.B. Mason, AIChE Symp. Ser. 75 (188) (1979) 1.
[7] J. Roiron, E. Garcin and F. Luck, Catal. Today 17 (1993) 311.
[8] J. Roiron, Nitrogen 88, Geneva, March 1988.
[9] J. Roiron, E. Garcin and F. Luck, Nitrogen 91, Copenhagen, June 1991.
[10] J.Y. Derrien, L. Seigneurin, French Patent 2450784, assigned to Rhône-Poulenc.
[11] M. Farber and S.P. Harris, J. Phys. Chem. 88 (1984) 680.
[12] I.N. Nam and J.R. Kittrell, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 186.