Laurence Udron
Marius Hackel [1]
Georg Schaub
Engler-Bunte-Institut
Universität Karlsruhe (TH)
D-76128 Karlsruhe, Germany
ludron@hotmail.com
hackel@ebigek01.ciw.uni-karlsruhe.de
georg.schaub@ciw.uni-karlsruhe.de

Thomas Turek
Institut für Chemische Verfahrenstechnik,
Universität Karlsruhe (TH)
D-76128 Karlsruhe, Germany

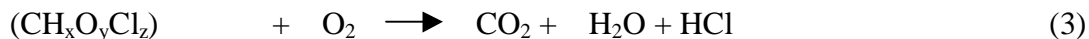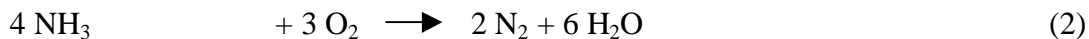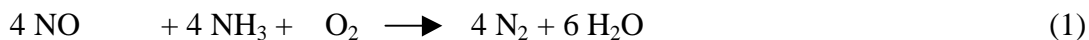[1] Person to whom correspondence should be sent

Catalysis of Reduction and Oxidation Reactions for Application in Gas Particle Filters

Keywords: gas cleaning in filters, catalytic reduction of NOx with NH_3 (SCR),
catalytic VOC oxidation

Introduction

Flue gases originating from biomass and waste incineration contain gaseous pollutants such as NOx, volatile organic compounds (VOC), SO_2, and others, that have to be removed. Catalytic processes are presently applied for selective reduction of NOx (SCR) and oxidation of dioxins in waste incineration, normally after a particle separation step. In this case, the dust-free gas passes through a honeycomb configuration allowing low pressure drop (Janssen 1997, Fahlenkamp et al. 1991, Hagenmaier and Mittelbach 1990).

NOx reduction can be seen to occur according to equation 1, at the same time the extent of a parallel oxidation of NH_3 with O_2 (equation 2) has to be minimized. Oxidation reactions of the variety of volatile organic compounds can be represented by equation 3. Catalysts commonly used in industrial applications are based on titania-supported vanadia (and tungsten) oxides.

$$4\,NO \quad + 4\,NH_3 + \; O_2 \longrightarrow \; 4\,N_2 + 6\,H_2O \tag{1}$$

$$4\,NH_3 \quad\quad\quad + 3\,O_2 \longrightarrow \; 2\,N_2 + 6\,H_2O \tag{2}$$

$$(CH_xO_yCl_z) \quad\quad + \; O_2 \longrightarrow \; CO_2 + \; H_2O + HCl \tag{3}$$

Integration of these catalytic reactions in gas particle filters has recently been proposed as an attractive solution, either separately for NOx reduction (e.g. Hübner et al. 1996, Saracco 1999) or for VOC oxidation (e.g. Saracco 1999, Gore 1999, Saracco and Specchia 1998). The simultaneous occurrence of reduction and oxidation reactions in a catalytic filter can be envisaged in the same way as it is proven in today's honeycomb reactors in waste incineration (Frings et al. 1994, Schaub 1996).

Objectives and Approach

The present study is a first part of an investigation addressing the simultaneous occurrence of oxidation and reduction reactions in catalytic filters. It has the objectives a) to assess the state of knowledge regarding suitable (types of) catalysts for reduction and oxidation, b) to collect and analyze published information about reaction rates of both NOx reduction and VOC oxidation, and c) to adjust a lab-scale screening method to the requirements of an activity test with various oxidation/reduction catalysts.

Results

Effects of simultaneous reduction and oxidation reactions with a V_2O_5/ZrO_2-Al_2O_3 catalyst were investigated experimentally by Jones et al. (1997) using a model flue gas with N_2, NO, NH_3, and Cl-Ethane as VOC model compound. For the conditions applied, complete conversion of NO was achieved in a fixed bed reactor at 300 °C, of chlorethane at 340 °C, both for a GHSV of 19000 h^{-1}. As can be seen in Figure 1, conversion-temperature profiles were practically identical for the separate reactions and the simultaneous reactions, indicating the absence of reciprocal kinetic effects. Here, a temperature window of about 80 K can be seen, in which both reactions exhibit complete conversion. In Figure 2, the same data are plotted together with data from a catalytic filter experiment using a V_2O_5/TiO_2-impregnated ceramic fiber filter material and a real flue gas (from fuel oil combustion, Hübner et al. (1996)). The range of conversions in these two literature sources reflects the strong variation in catalytic activities achieved (pure catalyst versus catalyst dispersed on ceramic filter material). In addition, the presence of H_2O and SO_2 in the case of the real flue gas may have deteriorated the catalytic activity. Other results by Hübner indicate that higher NO conversion values can be achieved with improved impregnation methods. The NO conversion - temperature curves exhibit characteristic maxima, which can be contributed to parallel NH_3 oxidation reactions with O_2 (reaction 2) and temperature effects on NH_3 adsorption.

Common industrial catalysts for SCR are based on titania-supported vanadia (and tungsten) oxides. Other possibilities of catalyst composition are described in the literature, indicating that any metal oxide active in SCR reactions could also be active in oxidation reactions. To combine both SCR and VOC oxidation reactions, a catalyst with regard to industrial application must a) operate under typical industrial space velocities (2000-15000 h^{-1}), b) be active in the presence of large amounts of water vapor, c) be resistant towards poisons (as sulfur or chlorine compounds), and d) be selective to produce N_2 and total oxidation products respectively (CO_2 and H_2O).

Various transition metal oxides and metals are active catalysts for both reactions:
- Iron and manganese oxides exhibit a high activity for SCR of NO with ammonia, even at low temperatures. However, these catalysts lead to N_2O as a byproduct, are sensitive towards SO_2 present in the gas and are poisoned by chlorine during VOC oxidation.
- Chromia catalysts exhibit the highest activity for VOC oxidation among the transition metals, however are not selective towards N_2 in SCR reactions. In addition, due to their toxicity, they do not appear suitable to be used for industrial applications.

- Copper-based catalysts are well recognized to be active and selective in both reactions. The main problem is the ability of copper to irreversibly form copper sulfate species in the presence of SO_2.
- Noble metals could be active catalysts for both SCR and VOC oxidation reactions. However, due to their poor resistance towards chlorine, they are unacceptable for chlorinated VOC removal or for VOC removal in gases containing HCl.
- Vanadia-type catalysts are well known to be active and selective in both SCR and dioxin removal and they exhibit a good resistance towards poisons. In spite of the cost and the toxicity of vanadia, it is presently considered to be the most interesting catalyst for SCR and VOC oxidation reactions. The amount of vanadia contained in the catalyst is significant for activity in a range up to 10 wt-%. Good dispersion of vanadia is necessary in order to increase the number of catalytically active species. Titania shows a strong interaction with vanadia. WO_3 in the catalyst is considered to stabilize the morphology of the support and inhibits the SO_2 into SO_3 oxidation reaction.

As for the selectivity of NOx reduction towards N_2, which is very significant for practical applications, measured values are collected in Figure 3, as affected by water vapor content in the gas. Undesired by-product in this case is N_2O. Increasing amounts of H_2O present in the gas improve the selectivity towards N_2, with a trend towards higher selectivities at lower temperature. These data are taken from various sources (Bosch et al. 1988, Lietti et al. 1996, Busca et al. 1998, Lintz et al. 1992, Sun et al. 2001) and confirm that with typical SCR catalysts and H_2O contents in flue gases, achievable selectivities towards N_2 are close to 100 %.

Rate equations capable to describe reaction kinetics of NOx reduction and VOC oxidation in a regime without significant transport limitations are listed in Table 1. This list originates from a collection of published investigations and presents a selection. The equations shown are being used in the current investigation. As an example, Figure 4 shows calculated conversion results for a range of GHSV from 2000 to 15000 h^{-1}, based on a kinetic analysis of data from Jones et al. (1997) and using rate equations 1-3, 1-4, and 1-5 in Table 1.

For the purpose of testing activities of various oxidation/reduction catalyst samples, fixed bed reactor procedures were defined in the present study for both reduction and oxidation. Figure 5 shows as an example results from these quick lab test experiments, using NO reduction and C_3H_8 oxidation as test reactions, for two $V_2O_5/TiO_2/WO_3$ catalysts with different V_2O_5 content (3 and 5.8 wt-%, respectively). For the same specific catalyst mass values applied (0.19 g $\cdot$ s/cm^3), C_3H_8 conversion curves are shifted towards higher temperatures (for about 200 K). This is a stronger effect than in the case of the VOC compound Cl-Ethane, as shown in Figure 1. Catalyst II (containing higher amounts of V_2O_5) exhibits higher activities in both cases. In the NO reduction case, no experiments at higher temperature (where NO conversion begins to decrease) were carried out. Those procedures will be used for ranking various catalyst samples, prepared according to different methods.

Conclusion and Outlook

The following conclusions can be drawn from the analysis of the available literature and from the own experiments and kinetic calculations carried out so far:

- Simultaneous catalytic reduction and oxidation reactions can occur on time scales of the order of seconds, as required for typical gas cleaning reactors,
- Characteristic maxima occur in NOx conversion versus temperature plots, due to parallel NH_3 oxidation reactions with O_2 and temperature effects on NH_3 adsorption,
- Time scales of VOC oxidation reactions vary with the kind of volatile organic compound (alkanes, aromatic hydrocarbons etc.),
- In $V_2O_5/TiO_2/WO_3$ catalyst systems, NOx reduction rates in general are higher than VOC oxidation rates,
- The limited published information available shows no significant reciprocal effects of simultaneous reduction and oxidation reactions,
- GHSV values achievable in ceramic filter materials impregnated with oxidation/reduction catalysts (as defined by gas inlet velocities and filter medium thickness) happen to be in the same order of magnitude as in typical catalytic honeycomb-type reactors.

In addition to the catalyst screening tests reported, a detailed kinetic investigation of simultaneous reactions occurring in catalytic fixed beds and in catalytic filter media will be carried out, using model flue gases and various model compounds.

Acknowledgements

References

Bosch, H., Janssen, F., 1988. Formation and Control of Nitrogen Oxides. *Catal. Today* 2: 369-532.

Busca, G., Baldi, M., Pistarino, C., Gallardo Amores, J.M., Sanchez Escribano, V., Finocchio E., Romezzano G., Breganil, F., Toledo, G.P., 1999. Evaluation of V_2O_5-WO_3-TiO_2 and Alternative SCR Catalysts in Abatement of VOCs. *Catal. Today* 53: 525-533.

Fahlenkamp, H., Mittelbach, G., Hagenmaier, H.P., Brunner, H., Tichaczek, K.-H., 1991. Katalytische Oxidation - Eine Technik zur Verminderung der PCDD-/PCDF-Emission aus Müllverbrennungsanlagen auf kleiner 0,1 ng TE/m^3 (i.N., tr.). *VGB Kraftwerkstechnik* 71 (7): 671-674.

Frings, B., Werner, K., 1994. Katalytische Dioxin-Minderung. *BWK/TÜ/Umwelt-Special.* Sonderdruck März 1994.

Gore, Remedia-Catalytic Filter System, product information (1999).

Hagenmaier, H., Mittelbach, G., 1990. Versuche zur katalytischen NOx- und Dioxinabbau im Abgas einer Hausmüllverbrennungsanlage. *VGB Kraftwerkstechnik* 70 (6): 491-493.

Hübner, K., Pape, A., and Weber, E.A., 1996. Simultaneous Removal of Gaseous and Particulate Components from Gases by Catalytically Activated Ceramic Filters, *Conf. Proc. High Temperature Gas Cleaning*, Edited by E. Schmidt, P. Gäng, T. Pilz, A. Dittler: 267-277.

Janssen, F.J., 1997. Environmental Catalysis - Stationary Sources. *In Ertl, Knözinger: Handbook of Heterogeneous Catalysis* 4: 1633-1668.

Jones, J., Ross, J.R.H., 1997. The Development of Supported Vanadia Catalysts for the Combined Catalytic Removal of the Oxides of Nitrogen and of Chlorinated Hydrocarbons from Flue Gas. *Catal. Today* 35: 97-105.

Lietti, L, Forzatti, P., 1996. *Heter. Chem. Rev.* 3: 33

Lintz, H.-G., Turek, T., 1992. Intrinsic Kinetics of Nitric Oxide Reduction by Ammonia on a Vanadia-Titania Catalyst. *Appl. Catal. A* 85: 13-25.

Saracco, G., Coupling Catalysts and High-Temperature Resistant Filters, Conf. Proc. High Temperature Gas Cleaning, Edited by A. Dittler, G. Hemmer, G. Kasper (1999) 627-640.

Saracco, G., and Specchia, V., 1998. Simultaneous Removal of Nitrogen Oxides and Flyash from Coal-based Power Plant Flue Gases. *Applied Thermal Engineering* 18: 1025-1035.

Schaub, G., 1996. Rauchgasreinigung mit Reststoffbehandlung und Wertstoffgewinnung in der Abfallverbrennung - Stand und Tendenzen. *Chemie Ingenieur Technik* 68: 1424-1431.

Schaub, G., Unruh, D., Wang, J., Turek, T., 2002. Kinetic Analysis of Selective Catalytic NOx Reduction (SCR) in a Catalytic Filter. *Chemical Engineering and Processing* (in press).

Stoll, M., Furrer, J., Seifert, H., Schaub, G., Unruh, D., 2001. Effects of Flue Gas Composition on the Catalytic Destruction of Chlorinated Aromatic Compounds with a V-oxide Catalyst. *Waste Management* 21: 457-463.

Sun, Q., Gao, Z., Chen, H., Sachtler, W., 2001. Reduction of NOx with Ammonia over Fe/MFI; Reaction Mechanism Based on Isotopic Labeling. *Journal of Catalysis* 134: 742-746.

Selected rate equations for catalytic reduction/oxidation reactions with vanadia-type catalysts

NOx reduction with NH$_3$

$$r_{NO-NH_3} \;=\; k_1 \, c_{NO} \hspace{6cm} \text{(1-1)} \hspace{1cm} \text{Beekmann and Hegedus 1991}$$

$$r_{NO-NH_3} \;=\; k_1 \, \frac{c_{NH_3} \, c_{NO}^{\,a}}{\left(1 + k_2 \, c_{NH_3}\right)\left(1 + k_3 \, c_{H_2O}\right)} \hspace{2cm} \text{(1-2)} \hspace{1cm} \text{Turek and Lintz 1992}$$

$$r_{NO-NH_3} \;=\; k_1 \, \frac{c_{NH_3}}{1 + k_2 \, c_{NH_3}} \; c_{NO} \hspace{4cm} \text{(1-3)} \hspace{1cm} \text{Schaub et al. 2002}$$

$$r_{NH_3-O_2} \;=\; k_1 \; c_{NH_3} \hspace{6cm} \text{(1-4)} \hspace{1cm} \text{Saracco and Specchia 1998}$$

VOC oxidation

$$r_{VOC-O_2} \;=\; k_1 \; c_{VOC} \hspace{6cm} \text{(1-5)} \hspace{1cm} \text{1)}$$

$$r_{VOC-O_2} \;=\; k_1 \; \frac{c_{O_2}^{\,a}}{1 + k_2 \, c_{H_2O}^{\,b}} \; c_{VOC} \hspace{3.5cm} \text{(1-6)} \hspace{1cm} \text{Stoll et al. 2001}$$

1) own assumption, based on experimental data by Fahlenkamp et al. 1991
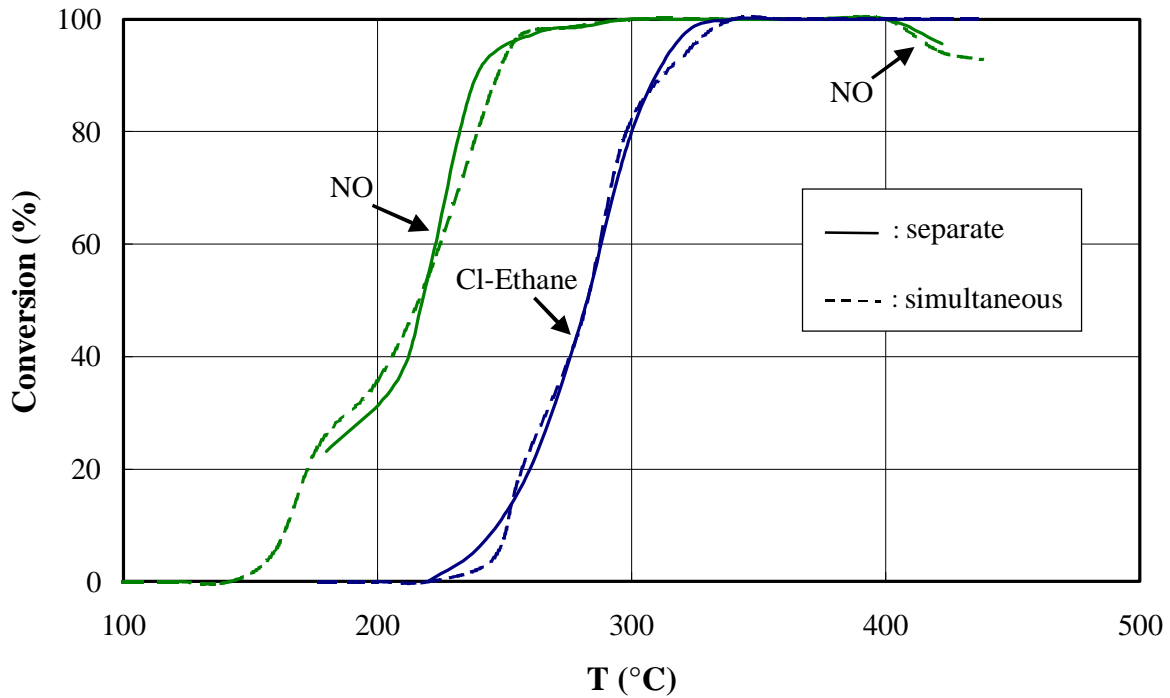
Fig. 1: Effect of simultaneous NOx reduction and VOC oxidation in catalytic fixed bed reactor experiments (Jones et al. 1997), $x_{NO\ in} = x_{NH3\ in} = 1000$ ppmv, $x_{Cl\text{-}Ethane\ in} = 700$ ppmv, $x_{O2\ in} = 3$ vol%, GHSV = 19000 h^{-1}
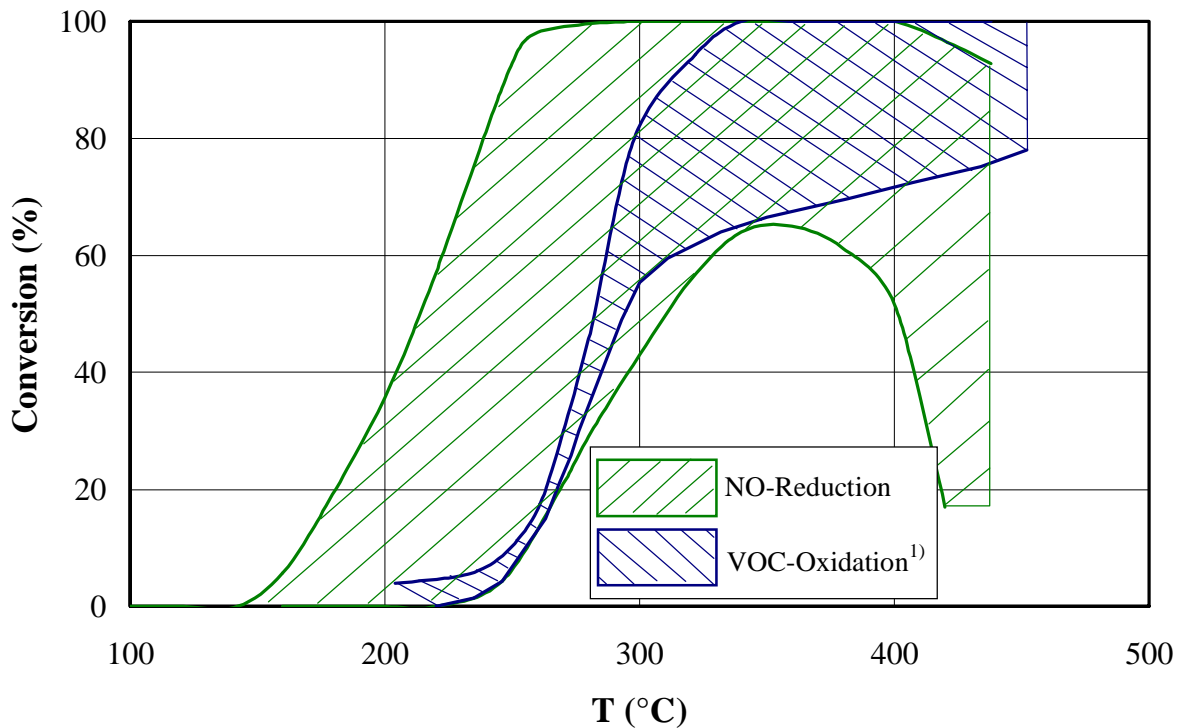
Fig. 2: Range of experimental data for simultaneous NOx reduction an VOC oxidation:
Jones et al. (1997):   fixed bed, $x_{NO\ in} = x_{NH3\ in} = 1000$ ppmv,
$x_{Cl\text{-}Ethane\ in} = 700$ ppmv, $x_{O2\ in} = 3$ vol%, GHSV = 19000 h^{-1}
Hübner et al. (1996): catalytic filter, $x_{NO\ in} = x_{NH3\ in} = 350$ ppmv, $x_{VOC\ in} = 55$ ppmv,
$x_{O2\ in} = 7.6$ vol%, GHSV = 11000 h^{-1} (+ SO_2, CO, CO_2)
[1]Cl-Ethane, $\sum$ VOC from fuel oil combustion
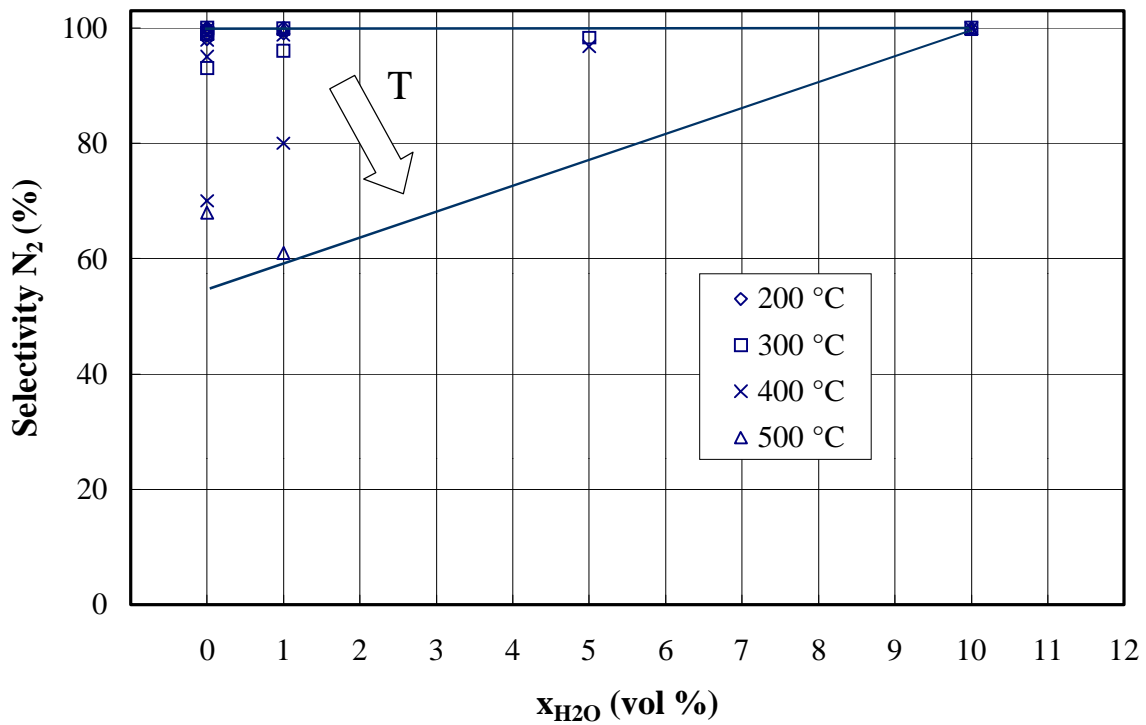
Fig. 3: Effect of water vapour content on selectivity for model flue gas based on different SCR catalysts (based on V_2O_5 and Fe_2O_3), range of GHSV: 5000 – 20000 h^{-1}, $x_{NO\ in}$, $x_{NH3\ in}$: 500 – 1030 ppmv, sources: see text
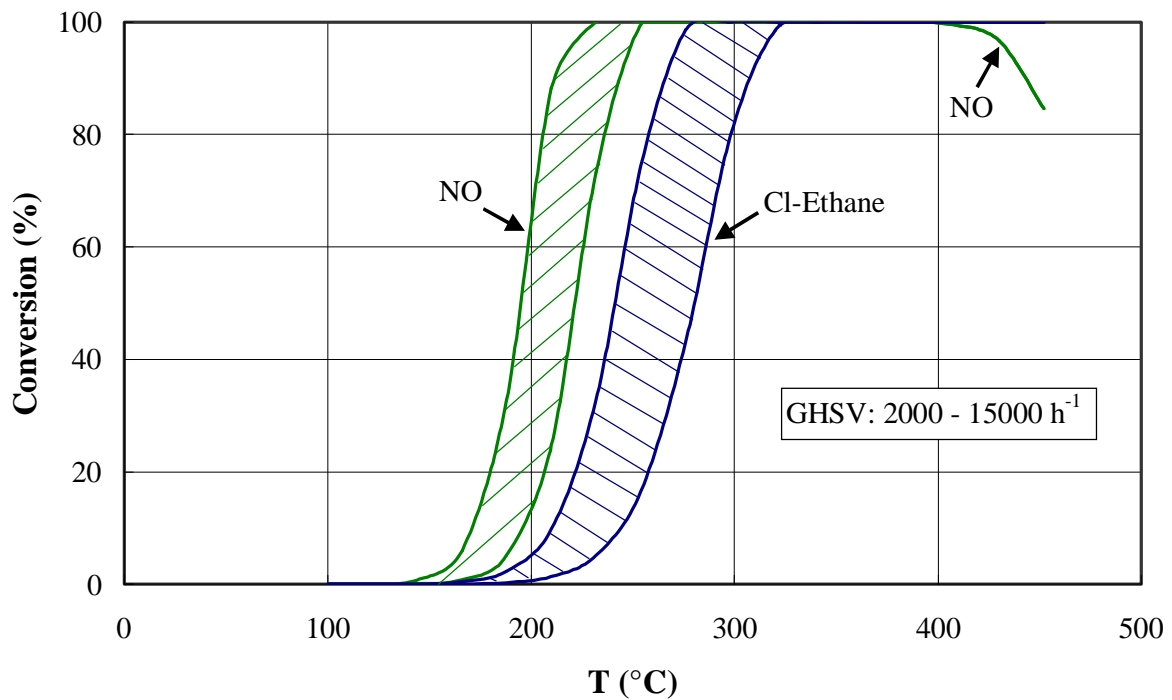
Fig. 4: Calculated conversion – temperature profiles, based on data from Jones et al. (1997), rate equations 1-3, 1-4, 1-5 in Table 1, variation of GHSV
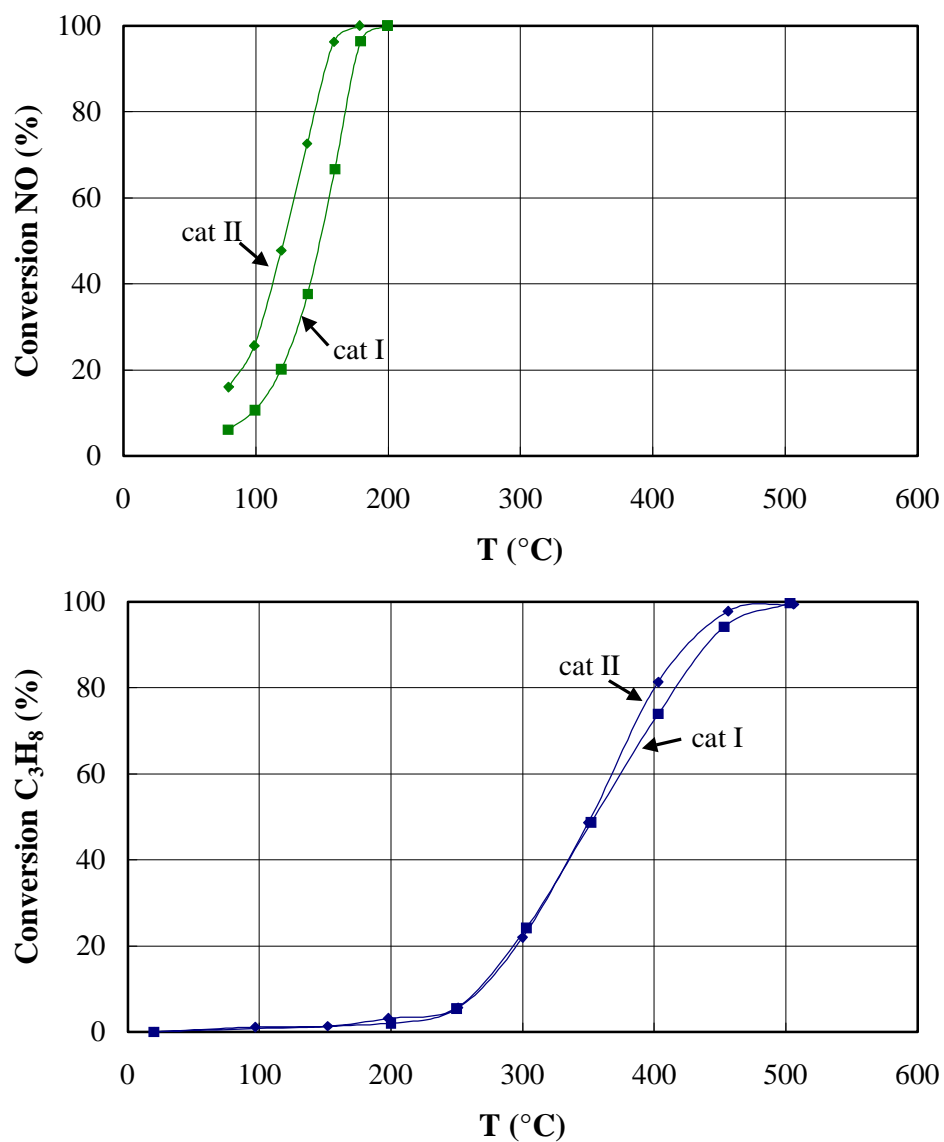
Fig. 5: Results from catalysts screening experiments in catalytic fixed bed reactors regarding NO reduction (top) and C_3H_8 oxidation (bottom), applying two different $V_2O_5/TiO_2/WO_3$ catalysts (V_2O_5 content 3 and 5.8 wt %),
$x_{NO\ in} = x_{NH3\ in} = 500$ ppmv, $x_{C3H8\ in} = 1000$ ppmv, $x_{O2\ in} = 3$ vol%,
$\dot{V}_{Gas\ n} = 93$ cm^3/min, $m_{cat} = 0.295$ g