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Ammonia oxidation into nitrous oxide over Mn/Bi/Al catalyst
II. Fluidized bed reactor experiments

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Abstract

The process of synthesis of nitrous oxide by ammonia oxidation in a fluidized catalyst bed reactor was studied using a suite of tools including both hardware and software. Pilot testing of the process was carried out in a fluidized bed reactor with a microspherical Mn/Bi/Al catalyst loaded therein. The experimental runs were guided by kinetic and simulation results. The stable operation regimes were achieved at the inlet ammonia concentration up to 45%; the selectivity for N_2O was 86–88% at the ammonia conversion of 98–99.5% in the optimal temperature range. The catalytic activity and the selectivity remained constant during pilot tests. The modeling data agreed with the experimental results.

Modeling of the large-scale reactor revealed that the catalyst productivity could be improved using the fluidized bed reactor in comparison to that in the tubular reactor due to the much more concentrated inlet flow. The inlet concentrations of ammonia could be much higher than that used in a tubular reactor (35–50 and 7–8%, respectively).

Keywords: Mn/Bi/Al catalyst; Ammonia oxidation; Nitrous oxide; Fluidized bed reactor; Pilot testing; Modeling; Large-scale reactor

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1. Introduction

Ever-growing use of nitrous oxide as a mild oxidizer for selective oxidation has given an impetus to development of high capacity and inexpensive technologies to produce nitrous oxide [1–4]. Recent studies have shown that nitrous oxide as a feedstock can be produced by direct oxidation of ammonia [5–6]. As shown by the studies performed by the Boreskov Institute of Catalysis in cooperation with Solutia Inc., selective oxidation of ammonia over Mn/Bi/α-Al_2O_3 catalysts is a promising way [2,7]. The studies were to solve such problems as the development of catalyst preparation procedure, mechanistic and kinetic characterization of the reaction, pilot testing of the process in fixed and fluidized catalyst bed reactors, design of industrial reactors and technological schemes.

Recent data on pilot testing of selective ammonia oxidation by air oxygen in a single-tube reactor as a model of a unit of an industrial multi-tubular reactor are reported elsewhere [8]. Ring catalysts are shown to provide steady-state technological regimes with the inlet ammonia concentration of 7–8% that corresponds to adiabatic temperature rise of ca. 600 °C. At the same time, a fluidized bed reactor seems more attractive for high capacity processes due to a potential considerable increase in the inlet ammonia concentration and simplifying the reactor design. For this reason the cooperative BIC-Solutia project is focused on investigations of Mn/Bi/Al catalyst performance in a fluidized bed reactor.

The aim of the present study was pilot testing of the setup with a fluidized bed reactor to synthesize nitrous oxide through ammonia oxidation over Mn/Bi/Al catalyst and evaluation of the main parameters and technological regimes for the industrial reactor. A number of chemical engineering tools including both hardware and software were used for accomplishment of the works such as: (a) kinetic studies, (b) mathematical modeling of the optimal catalyst activity and process parameters for the pilot reactor, (c) pilot runs at the maximal selectivity for nitrous oxide, (d) modeling of the large-scale reactor. The results obtained are discussed in the present paper.

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Table 1
Reaction conditions

Catalyst weight (g)	1–8
Temperature (°C)	315–370
Pressure (bar)	1
Contact time (s)	1–14
Inlet reagent concentrations	
Ammonia (vol.%)	17–45
Oxygen (vol.%)	17–55
Balance	Helium

2. Kinetic studies

Two laboratory setups were used during kinetic studies: plug flow reactor for preliminary investigation of catalyst sample properties and continuous tank reactor under stirring for study of kinetics. The chemical composition of microspherical catalysts prepared for studies in a fluidized bed reactor was identical to that of the macrospherical catalyst studied before in a fixed bed reactor. In the catalyst samples, the particles were 10–120 μm in size with the fine fraction (<40 μm) content of about 20%.

A number of kinetic experiments were carried out in an isothermal plug flow reactor under various reaction conditions (see Table 1) to study properties of the microspherical catalyst.

The influence of reagent concentrations and operation temperature on the intrinsic rate of ammonia conversion and selectivity for products was studied. In spite of high concentrations of ammonia, the dependences were shown to be similar to those of the macrospherical catalyst [8]. The selectivity for nitrous oxide decreased with an increase in the ammonia concentration but increased as the concentrations of oxygen and water increased. In all the range of operation conditions, the selectivity for nitrous oxide increased with ammonia conversion due to lowering of the ammonia concentration and generation of water. The optimal temperature fell into the interval of 330–360 °C to achieve maximal selectivity for nitrous oxide. These temperatures also were close to the optimal temperatures observed with the macrospherical catalyst [8].

The selectivity for N_2O reaches 88–89% at almost complete conversion of ammonia at excess oxygen in the inlet flow, even at the inlet ammonia concentration up to 44–46%. A minor decrease in the selectivity is observed with the inlet gas containing oxygen in a substoichiometric amount. Fig. 1 and Table 2 illustrate typical results of the catalyst testing. The selectivity for nitrogen oxide corresponding to the inlet ammonia concentration of 44–46% is 0.01–0.03% but not higher than 0.5% at any experimental conditions.

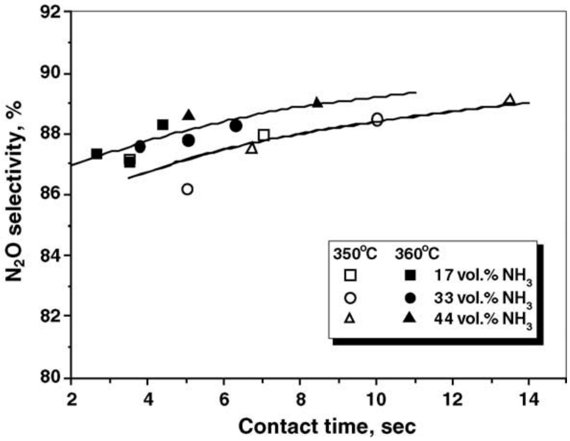

Fig. 1. Results of catalyst testing in bench scale setup.

A series of experiments were performed using a continuous tank reactor under stirring to develop kinetic model for reactor simulation. The catalyst for these studies was prepared the same way as the industrial catalyst. One-parameter dependences of the reaction rates were obtained by varying concentrations of NH_3, O_2 and H_2O at otherwise constant parameters.

There were 133 kinetic runs to obtain the whole set of experimental data for the regression analysis. The kinetic data were analyzed on the basis of the reaction pathway including two main reactions – formation of nitrous oxide and nitrogen. The rates of NO and NO_2 formation were assumed equal to zero due to the low NO concentration and the absence of NO_2 in the outlet gas mixture. The following steps could be used to describe the ammonia transformations [8]:

$$2NH_3 + 2O_2 = N_2O + 3H_2O$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \tag{1}$$

Mathematical processing of the experimental data allowed kinetic equations to be suggested for the rates of product formation by reactions (1). Non-linear regression of a number of phenomenological kinetic equations for nitrous oxide and nitrogen formation rates was performed. The available information about the reaction mechanism, in particular about the

Table 2
Kinetic study results

Temperature (°C)	Inlet concentration (vol.%)		Ammonia conversion (%)	Nitrous oxide selectivity (%)	Nitrogen oxide selectivity (%)
	NH_3	O_2			
350	17.0	18.0	87.7	87.2	0.24
	33.1	34.3	87.9	86.2	0.05
	44.7	55.3	97.3	89.1	0.03
360	17.4	17.8	89.4	87.1	0.5
	45.0	55.0	94.6	89.0	0.01

correlation between the selectivity for N_2O and the portion of manganese with more oxidized state on the catalyst surface, was used to derive a number of kinetic rate expressions [9]. Discrimination of 20 types of kinetic models made it possible to reveal the most accurate and reliable kinetic equations.

The minimal disagreement between experimental and calculated data on the most statistically reliable parameters was found for the Langmuir–Hinshelwood type kinetic equations. They were obtained based on the hypothesis that ammonia is oxidized to nitrous oxide and to nitrogen on the active sites in different oxidation states. The kinetic rate expressions with the values of the activation energies and pre-exponential constants provided the goodness of fit and they are proprietary [10]. The average deviation was no more than 10% in all experimental points, for example the average description error equalled 1% for the selectivity for nitrous oxide.

3. Mathematical model

There were two steps of modeling: (1) simulation of operation regimes in a pilot reactor with catalyst volume of 1–10 l, and (2) numerical investigation of large-scale reactor performance (catalyst volume up to 100 m^3). The two-phase model in the generalized formulation was used for isothermal conditions for procedures of fluidized bed modeling [11] due to different hydrodynamics in differently scaled reactors. The material balance for dense and bubble phases may be expressed as follows:

$$u_\mathrm{b}\frac{\mathrm{d}C_\mathrm{bi}}{\mathrm{d}l}+\frac{k}{\varepsilon_\mathrm{b}}(C_\mathrm{bi}-C_\mathrm{ei})-D_\mathrm{zb}\frac{\mathrm{d}^2C_\mathrm{bi}}{\mathrm{d}l^2}+\rho_\mathrm{b}aR_\mathrm{i}=0$$

$$u_\mathrm{e}\frac{\mathrm{d}C_\mathrm{ei}}{\mathrm{d}l}+\frac{k}{(1-\varepsilon_\mathrm{b})\varepsilon_\mathrm{e}}(C_\mathrm{ei}-C_\mathrm{bi})-D_\mathrm{ze}\frac{\mathrm{d}^2C_\mathrm{ei}}{\mathrm{d}l^2}+\rho_\mathrm{e}aR_\mathrm{i}=0 \tag{2}$$

with boundary conditions:

$$l=0:\ D_\mathrm{ze}\frac{\mathrm{d}C_\mathrm{ei}}{\mathrm{d}l}=u_\mathrm{e}(C_\mathrm{ei}-C_\mathrm{i}^0)$$

$$D_\mathrm{zb}\frac{\mathrm{d}C_\mathrm{bi}}{\mathrm{d}l}=u_\mathrm{b}(C_\mathrm{bi}-C_\mathrm{i}^0)$$

$$l=L:\ \frac{\mathrm{d}C_\mathrm{ei}}{\mathrm{d}l}=0,\ \frac{\mathrm{d}C_\mathrm{bi}}{\mathrm{d}l}=0$$

The model parameters were estimated at each step using literature data and the data obtained by cold flow studies. Such model parameters as interphase mass transfer coefficient, gas axial dispersion in both phases and void phase density were estimated from the available literature data covering both the bubbling and turbulent regimes [11,12]. Void fraction at given gas velocity and transition conditions from bubbling to turbulent fluidization were evaluated from the data of cold flow studies [13].

The pilot reactor modeling provided information about the process behavior under different operating conditions and also permitted the evaluation of optimal conditions for experimental runs. Operation regimes were simulated to realize the process with the inlet ammonia concentration as high as possible. The modeling procedure included the following steps: (a) simulation of concentration profiles along the bed height for the reagents (ammonia, oxygen, water) and the products (nitrous oxide and nitrogen); (b) identification of test conditions in the pilot reactor for catalysts with different activities; (c) evaluation of the optimal catalyst activity for pilot runs at a high inlet concentration of ammonia and a given temperature; (d) comparison of the experimental data and calculated results.

The primary goal of the second modeling stage was to investigate the influence of hydrodynamics and operation conditions on the performance of the large-scale reactor. The modeled concentration profiles permitted the dependence of nitrous oxide selectivity and reactor size on hydrodynamic parameters such as interphase mass transfer and gas axial dispersion to be revealed. The optimal technological regimes were determined using the results obtained by modeling in order to minimize the reactor dimensions and maximize the catalyst productivity.

4. Experimental runs

The main goals of pilot tests were:

- To study the catalyst performance in a pilot fluidized bed reactor and to identify the influence of operation conditions on the process parameters such as ammonia conversion and selectivity for nitrous oxide;
- To achieve the stable operation regimes at optimal temperature range with a high inlet concentration of ammonia and to study the catalyst stability;
- To identify the optimal range of process conditions in order to scale-up the reactor.

4.1. Reactor schematic

Experimental studies were carried out in two kinds of setup where the inner diameters of the reactors were 4.0 and 6.4 cm. Fig. 2 illustrates the main features of fluidized bed reactors. Heat exchangers were arranged around each reactor tube with a loaded catalyst to control temperature in the catalyst bed. Thermocouples for measurement of the inbed temperature were mounted along the height in horizontal tubes extended through the reactor wall and into the fluidized bed. Notice that close to isothermal operation regimes were used for all pilot test runs. Temperature gradients inside the fluidized bed were no more than 3 °C.

Internal removable screens were installed in the reactors to vary interphase mass transfer and to elucidate the effect of fluid bed hydrodynamics on the catalyst performance. A series of experiments was performed without screens.

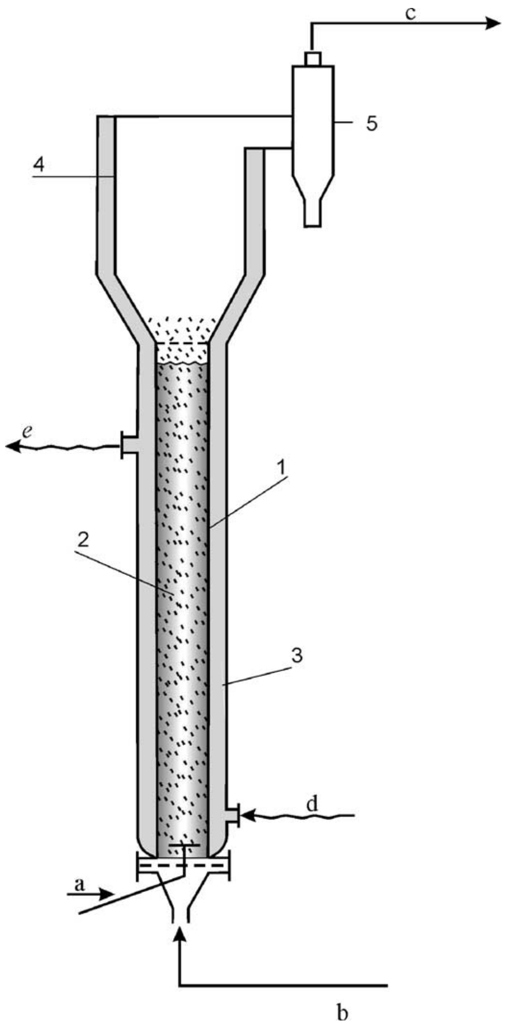

Fig. 2. Pilot reactor scheme: (1) reactor tube, (2) catalyst bed, (3) heat exchanger, (4) separator, (5) cyclone, (a) ammonia feed, (b) feed of oxygen, steam and helium (nitrogen), (c) reaction mixture outlet, (d and e) heat carrier.

A gas feeding system consisted of two units. Oxygen with an inert gas (helium or nitrogen) was supplied to the reactor bottom, water was added in some experiments. Ammonia was supplied to the bed separately from oxygen through a sparger, the isolated line for ammonia supply prevented the formation explosive gaseous composition outside the catalyst bed.

4.2. Pilot reactor modeling

In considering the reactor diameter and the flow rate limitations imposed by the small size of the catalyst particles, the bubbling fluidization regime with small bubbles was expected in the pilot reactor. The available literature data [11,12] and the data obtained by cold flow studies allowed the following assumptions for the pilot reactor modeling: (1) the gas pressure is constant along the reactor length; (2) gas axial dispersion is negligible in both dense and bubble phases; (3) the bubble phase is free of catalyst particles; (4) gas velocity in the dense phase equals the minimal fluidization velocity. The parameters varied during simulation were the inlet concentration of ammonia, the coefficient of catalyst activity, catalyst bed height, superficial gas velocity, catalyst bed temperature.

The reactor modeling demonstrates that pilot runs can be conducted in the optimal temperature range provided that the inlet ammonia and oxygen concentrations are fed in a close to stoichiometric ratio. To achieve the operation regimes at a given temperature, the optimal range of the catalyst activity is chosen on the basis of: (a) restrictions on gas velocity, (b) calculated data on the catalyst loading and the reaction heat evolution, (c) restrictions on the heat exchanger system. Entrainment of the catalyst particles is prevented using the superficial velocity not higher than the terminal particles velocity [13].

Fig. 3 illustrates the results obtained with the catalysts of different activities. One can see that the intrinsic activity of the microshpherical catalyst for pilot tests should be significantly lower than that of the macrospherical catalyst in order to minimize the specific heat evolution in the bulk of the fluidized catalyst bed. At the optimal temperature, the operation

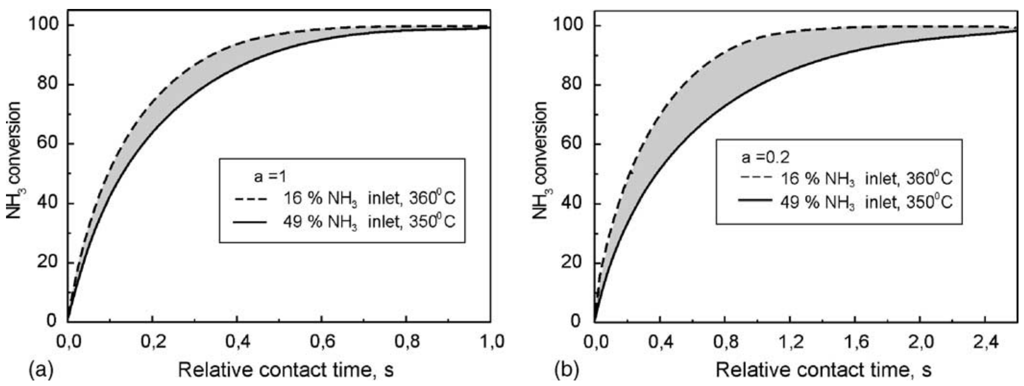

Fig. 3. Ammonia conversion calculated for pilot reactor with different catalyst activity: (a) catalyst activity corresponds to intrinsic activity of macrospherical batch, the coefficient of activity is equal to 1; (b) optimal activity of microspherical batch for pilot tests, the coefficient of activity is equal to 0.2.

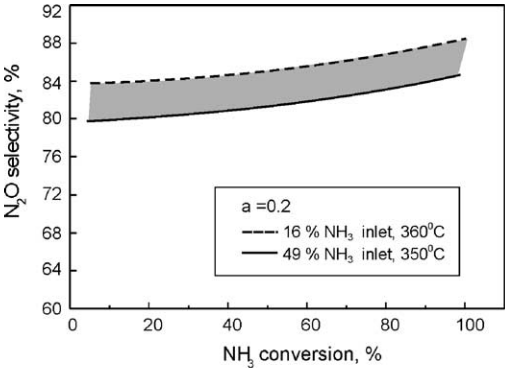

Fig. 4. N_2O selectivity vs. ammonia conversion in a pilot reactor.

regimes can be achieved at the selectivity for nitrous oxide equal to 83–88% at a high ammonia conversion (Fig. 4).

Simulation of the pilot reactor allowed the optimal catalyst activity, catalyst loading and the optimal ranges of temperature, pressure and gas velocities to be determined. Thus, whole range of pilot conditions was chosen on the basis of intrinsic catalyst properties and modeling results.

Pilot setups were carried out in the Solutia Inc. (Houston and Pensacola, USA). Two series of runs were performed under operating conditions given in Table 3:

- Series 1. Influence of operation conditions: temperature, interphase mass transfer and inlet feed composition were investigated in a 4.0 cm ID reactor.
- Series 2. Catalyst stability tests were carried out in a 6.4 cm ID reactor.

4.3. *Influence of process parameters*

The parameters varied during the experimental Series 1 were: catalyst bed loading, superficial gas velocity, catalyst bed temperature, inlet concentration of ammonia, oxygen and water, interphase mass transfer rate. The influence of the reaction conditions on the process characteristics was studied to meet to the main goals of pilot tests. The optimal operation regimes were chosen to achieve as high as possible ammonia conversion and selectivity for nitrous oxide and a low selectivity for nitrogen oxide. One-parameter dependences obtained at otherwise identical parameters revealed the effects of temperature, interphase mass transfer, reagent concentrations. More than 100 experimental points were measured during pilot runs.

Table 3
Operation conditions

Gas velocity (cm/s)	0.1–0.2
Temperature (°C)	330–380
Pressure (atm)	2
Inlet concentrations	
Ammonia (vol.%)	17–46
Oxygen (vol.%)	17–55
Water (vol.%)	0–33
Helium (nitrogen)	Balance
Total time of pilot tests (h)	>1000

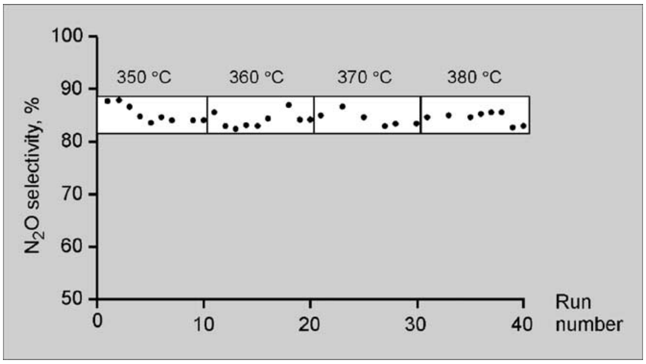

Fig. 5. Temperature effect on N_2O selectivity in pilot runs at inlet NH_3 concentration of 17–18%.

4.4. *The influence of temperature*

The temperature effect was studied at constant pressure, catalyst loading, and inlet gas composition. Screens were mounted in the catalyst bed. The optimal operation temperature in the pilot fluidized bed reactor was determined from the following conditions: the maximal ammonia conversion at a given catalyst loading and no decrease in the selectivity for nitrous oxide. The operation temperature was varied from 330 to 380 °C at 10 °C intervals. Almost complete ammonia conversion was achieved at temperatures higher than 340 °C.

Fig. 5 illustrates the influence of temperature on the selectivity for nitrous oxide. In all the experimental points in the figure, ammonia conversion is higher than 95%. A number of runs show only a minor effect on the selectivity for N_2O within this temperature range. Elevation of the operation temperature from 350 to 380 °C resulted in an increase in the ammonia conversion up to 100% and a slight decrease in the selectivity for N_2O. All the runs demonstrated that the optimal temperature range to achieve the maximal N_2O selectivity was identical to that determined in a laboratory reactor with the microspherical catalyst.

4.5. *The influence of inlet concentrations*

The runs also were carried out in the reactor with screens. Figs. 6–8 present some selected data. One-parameter effect was studied by varying the inlet ammonia concentration from 17 to 45% at otherwise identical operation conditions. To prevent a decrease in the N_2O selectivity, the oxygen concentration in the inlet reaction mixture was maintained in no less than the stoichiometric amount.

The catalyst activity as a function of inlet ammonia concentration was characterized using relative contact time required to achieve the given ammonia conversion (see Fig. 6). The catalyst activity in the fluidized bed is seen here to decrease significantly with an increase in the ammonia concen-

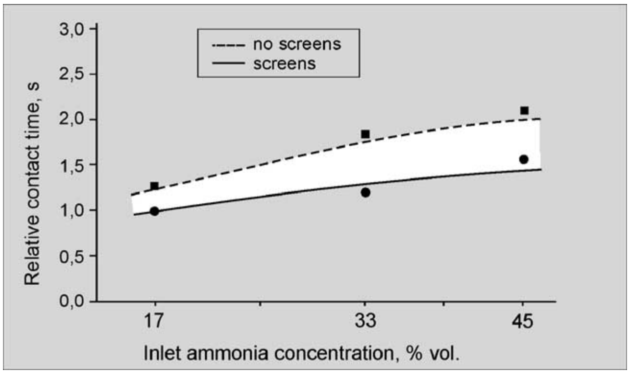

Fig. 6. Effect of interphase mass transfer on the contact time required to achieve given ammonia conversion at temperature of 360 °C, lines – calculated data, points – experimental points.

tration in the system. An increase in the inlet water concentration also resulted in a decrease in the catalyst activity. The same effect was shown while studying the intrinsic catalyst properties for this reaction.

Fig. 7 presents a set of experimental data on the selectivity for N_2O obtained in the reactor with screens at temperatures of 350 and 360 °C and a steam-free inlet reaction mixture. As mentioned above, these temperatures are optimal to obtain the high selectivity for N_2O. All experimental points correspond to high ammonia conversions (>95%). The N_2O selectivity as high as 84–88% was observed within the whole range of the inlet ammonia concentrations under study. Addition of steam to the catalyst bed caused a slight increase in the selectivity for N_2O (Fig. 8).

4.6. *The influence of interphase mass transfer*

The first experimental results given above were obtained using a reactor with screens mounted into the catalyst bed. The screens were used in order to decrease bubbles in size in the pilot reactor and to promote the interphase mass transfer. According to the literature data [11,13] and our experimental results, small bubbles are generated in such a reactor, and the mass transfer rate between bubbles and dense phase is rather high. To study the catalyst performance at different transfer rate, the screens were removed. As a result the mass transfer rate was decreased and the experimental runs were continued in the reactor with free catalyst bed. Figs. 6 and 8 show examples of experimental data at 360 °C.

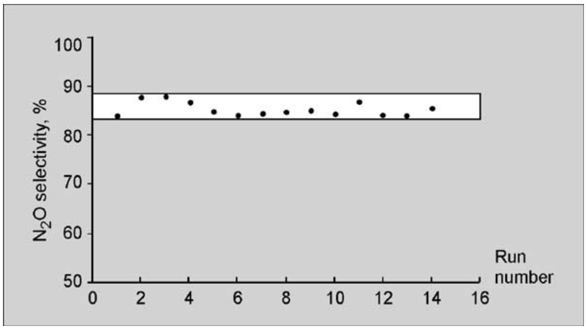

Fig. 7. Comparative data of N_2O selectivity in pilot runs with screens. Experimental points are presented for inlet ammonia concentration of 17–45% and temperature of 350 and 360 °C. Simulated data: upper line – inlet ammonia concentration of 17%, temperature of 360 °C; lower line – inlet ammonia concentration of 45%, temperature of 350 °C.

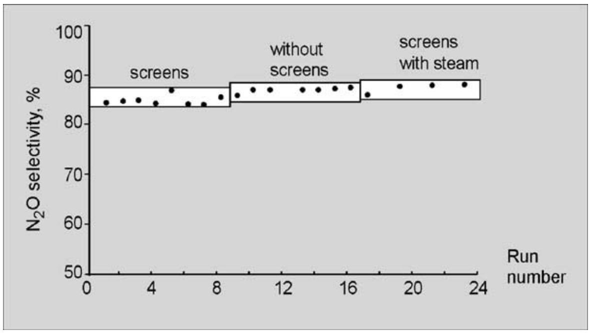

Fig. 8. Effect of interphase mass transfer at temperature of 360 °C. Experimental points are taken from runs with inlet ammonia concentration of 17–34%. Upper and lower lines were calculated for inlet NH_3 concentration of 17 and 34%, correspondingly.

The results obtained with and without screens revealed the influence of the interphase mass transfer on the apparent catalyst activity and selectivity. When the screens were removed, an increase in the mass transfer resistance was usually followed by an evident decrease in the apparent catalyst activity (Fig. 6).

The selectivity for nitrous oxide was practically not altered after the screens removal (Fig. 8). A minimal perceptible increase in the selectivity was observed in the screen-free reactor that led to conclude that the selectivity for nitrous oxide depended only slightly on the mass transfer rate. Notice that this kind of influence of the mass transfer resistance on the selectivity for the target product is not ordinary. Lowering of selectivity for the target product with the decrease in mass transfer rate is usually observed in the case of selective oxidation of hydrocarbons in fluidized bed reactors and moreover, the selectivity decreases more sharply with an increase in the catalyst activity [14].

The slight increase in the selectivity towards the target product on decreasing mass transfer resistance for selective oxidation of ammonia can be accounted for by the following kinetic features: there are no consecutive reactions of N_2O consumption (see reaction scheme (1)), and the ammonia concentration in the dense phase decreases with the growth of bubbles in size that leads to improvement of the selectivity for N_2O. This effect is expected to be stronger in a large-scale reactor in bubbling mode.

4.7. *Stability tests*

Two methods were used to study the catalyst stability; these were direct stability tests of the catalyst in the fluidized bed reactor with 6.4 cm ID and comparison of the activity and N_2O selectivity of the samples before and after experiments

Table 4
Examples of results of stability tests

Temperature (°C)	364	365
Inlet concentrations (mol.%)		
Ammonia	32.8	31
Oxygen	33.2	31
Reactor inlet flow, 1/min	20	16
Run time (h)	81	86
Ammonia conversion – in 2 h of run (%)	86.0	88.9
Ammonia conversion – at the end of run (%)	88.5	88.3

in the 4.0 cm ID reactor. The properties of the fresh and used samples were tested in a laboratory plug flow reactor.

Operating conditions and the results of direct stability tests are shown in Table 4.

The initial catalyst loading was constant during direct stability tests with no fresh catalyst added to the reactor. The run time was about 700 h in total. The differences between initial and final catalyst characteristics were less than 3% for ammonia conversion and less than 0.3% for the selectivity for N_2O.

The similar results were obtained in comparison of intrinsic properties of the catalyst tested in the 4.0 cm ID reactor. Table 5 gives the comparative results obtained at 350 °C.

4.8. *Comparison of modeling and experimental data*

Figs. 6–8 illustrate the comparative results on the catalyst activity and selectivity for nitrous oxide obtained during pilot runs and derived from simulation of pilot operation regimes. As mentioned in Section 4.4, the contact time required to achieve the given ammonia conversion was used to characterize the catalyst activity as a function of inlet concentration of ammonia (Fig. 6). The figure shows the data on pilot tests in the screen and screen-free reactors. The results of modeling indicate a decrease in the apparent activity of the catalyst due to an increase in the inlet ammonia concentration and screens removal.

The experimental and calculated selectivities for N_2O in the reactor with screens are compared in Fig. 7. The area between the upper and lower straight lines is the range of simulated selectivity for N_2O under different operation conditions. The upper line corresponds to the inlet ammonia concentration of 17% and complete ammonia conversion, the line under experimental points corresponds to inlet 45% NH_3 concentration and 95% ammonia conversion. All experimental values of N_2O selectivity located within the calculated interval correspond to the ammonia conversion higher than 95%. It is seen in Fig. 7 that the results obtained in pilot tests agree well with the modeling results, the difference between experimental and simulated values is no more than 3–4% for all runs. The simulated results describe adequately the influence of mass transfer resistance and steam (Fig. 8).

Thus, the applied mathematical model describes correctly the influence of process and hydrodynamic parameters on the catalyst behavior in a pilot fluidized bed reactor. The modeling data agree enough with the experimental data.

5. Large-scale reactor design

Mathematical modeling was used to study the effect of hydrodynamics in a large-scale fluidized bed reactor. The operation regimes were simulated using the mathematical model in the generalized formulation (2). The hydrodynamic parameters applied for reactor scaling-up were evaluated based on literature data and results of cold flow studies [11–13]. Special attention was paid to the technical restrictions on the heat removal system. The optimal technological regimes were chosen by considering the important factors such as process characteristics, catalyst volume, scaling up problems, technological scheme and others.

The gas axial dispersion in the dense phase was shown to affect moderately the reactor performance. Neglecting axial dispersion leads to 10% decrease in the calculated bed height providing the ammonia conversion of 98% and to a decrease in the calculated selectivity by 1% (Fig. 9). The modeling results also indicate a minor effect of the mass transfer resistance on the selectivity for N_2O obtained in the pilot reactor. Though hydrodynamic conditions differ greatly, the calculated N_2O selectivity in a large-scale reactor also increases with a decrease in the mass transfer rate (Fig. 10). The increasing mass transfer resistance decreases NH_3 concentration in the dense phase thus leading to an increase in the N_2O selectivity. The inlet reaction mixture of 51 vol.% NH_3 and 49 vol.% O_2 was found to be suitable for the fluidized bed reactor operation.

Modeling enables to estimate the optimal catalyst activity, reactor dimensions, technological regimes and catalyst productivity for large-scale fluidized bed reactors. In spite of restrictions on the specific area of the cooling system, stable operation regimes can be achieved with the adiabatic temperature rise up to 3500 °C.

Table 5
Comparative tests of fresh and used catalyst samples

Catalyst weight (g)	Inlet composition (vol.%)		X_{NH_3} (%)	S_{N_2O} (%)	S_{NO} (%)
	C_{NH_3}	C_{O_2}			
Fresh	33.1	34.3	87.9	86.2	0.05
Used	33.6	34.1	86.0	89.2	0.03
Fresh	46.4	53.6	86.2	87.5	0.03
Used	45.0	55.0	86.2	89.6	0.02

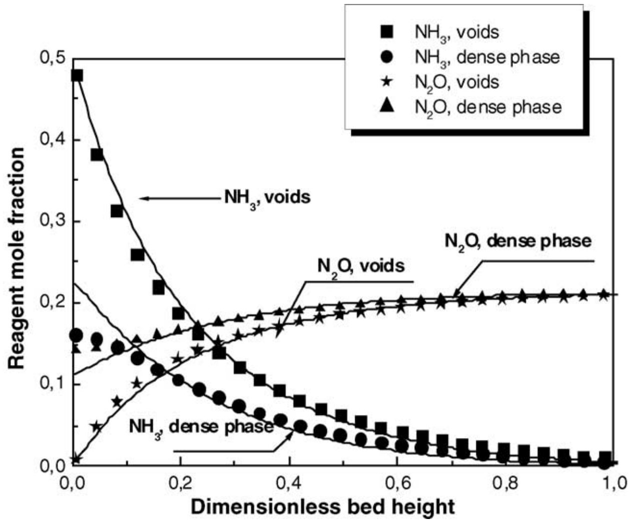

Fig. 9. Modeling of axial profiles of reactant concentrations in a large-scale reactor. Solid lines stand for $D_z = 0$, symbols for $D_z = 3.0\,m^2/s$.

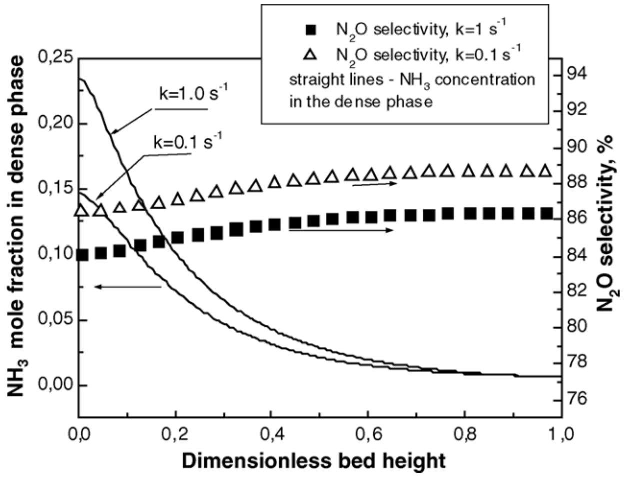

Fig. 10. Modeling of interphase mass transfer influence on N_2O selectivity in a large-scale reactor.

As a result, appropriate operation regimes in the large-scale reactor are chosen for further economic evaluations. The reactor was designed for units of the capacity up to 1.3×10^5 t/year of pure N_2O. Table 6 illustrates main comparative characteristics of tubular and fluidized bed reactors of a given capacity.

Table 6
Reactor characteristics with annual capacity of 1.3×10^5 t_{N_2O}/year

Type of reactor	Tubular	Fluidized bed
Catalyst particle dimension (mm)	5–7	0.01–0.12
Inlet ammonia concentration (vol.%)	5–8	33–50
Adiabatic temperature rise (°C)	550–650	2500–3500
Catalyst volume (m^3)	120	40
Productivity of a weight unit ($t_{N_2O}/t_{cat.}$/day)	4–5	7–8
Number of reactors	3	1

6. Conclusion

Nitrous oxide production via selective ammonia oxidation on Mn/Bi/α-Al_2O_3 catalysts has been tested in pilot fluidized bed reactor setups. The following main conclusions summarize the results of pilot runs:

- The inlet reaction mixture with ammonia concentration as high as 45% is appropriate for operation of a fluidized bed reactor.
- Typical selectivity for nitrous oxide of 84–88% is achieved in the setup with a fluidized bed reactor at ammonia conversion of 95–99.5%, selectivity for NO being not higher than 0.5%.
- The interphase mass transfer resistance is shown not to detriment the selectivity for nitrous oxide, a slight growth of the selectivity for N_2O being observed on decreasing the mass transfer rate.
- A good agreement between the experimental and modeling data is demonstrated.
- The microspherical catalyst is shown to be stable enough, both the catalytic activity and selectivity being constant during the pilot tests.

Mathematical modeling provides information about the catalyst behavior in respect to different process and hydrodynamic conditions in a large-scale reactor and also allows the optimal regimes for achieving a high selectivity for nitrous oxide to be established. It is expected that the experimental effects revealed during pilot tests and supported by simulation will be identical to those in a large-scale reactor.

Identical levels of activity and selectivity for nitrous oxide are expected in the commercial reactor according to modeling results. Application of a fluidized bed reactor in comparison with a tubular one enables to enhance the catalyst productivity and maximal single train capacity due to much higher concentrated feed. The inlet concentrations of ammonia can be much higher than that used in a tubular reactor (35–50 and 7–8%, respectively).

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