

# 1 **N<sub>2</sub>O catalytic decomposition – from laboratory experiment to industry reactor**

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7

## 8 **Abstract**

9 Paper deals with design of pilot reactor for low temperature N<sub>2</sub>O decomposition in off-gases  
10 from HNO<sub>3</sub> production. Pseudo-homogeneous one-dimensional model of an ideal plug flow  
11 reactor was used for modeling of N<sub>2</sub>O decomposition in a laboratory fixed bed reactor filled with  
12 grains or pellets of a Co-Mn-Al mixed oxide catalyst. Increase in inlet pressure up to 0.6 MPa  
13 did not influence the effective diffusion coefficient, but improved the achieved N<sub>2</sub>O conversion.  
14 Based on the laboratory data of N<sub>2</sub>O decomposition over Co-Mn-Al mixed oxide pellets, catalyst  
15 bed of 3400 kg was estimated for target 90 % N<sub>2</sub>O conversion (30 000 m<sup>3</sup> h<sup>-1</sup> of exhaust gases  
16 from HNO<sub>3</sub> plant containing 0.1 molar% N<sub>2</sub>O, 0.01 molar% NO, 0.01 molar% NO<sub>2</sub>, 3 molar%  
17 H<sub>2</sub>O, 5 molar% O<sub>2</sub>) at 420 °C and 600 kPa inlet pressure.

18

19 **Key words:** N<sub>2</sub>O, Catalytic decomposition, Fixed bed reactor, Effectiveness factor, Mixed oxide  
20 catalysts

21

## 22 **1. Introduction**

23 In the last years, the catalytic decomposition of N<sub>2</sub>O as a method for abatement of N<sub>2</sub>O  
24 emissions in waste gases attracted increasing attention due to the expected inclusion of N<sub>2</sub>O in  
25 the greenhouse gas trade. Besides Fe-zeolites [1-4] and Rh containing catalysts [5, 6], Co-spinels  
26 [7-10] seem to be promising catalysts for this reaction at temperatures below 450 °C. Among

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27 them, the Co-Mn-Al mixed oxide with spinel structure (Co:Mn:Al = 4:1:1) prepared by thermal  
28 treatment of layered double hydroxide (LDH) precursors was active [11] and stable in the  
29 presence of O<sub>2</sub>, H<sub>2</sub>O and NO<sub>x</sub> [12]. Our effort to increase further catalytic activity of the  
30 mentioned catalyst led us to the study of the effect of low amounts of promoter incorporation  
31 into the catalyst. Alkali promoters, especially potassium, improved catalytic performance  
32 dramatically [12, 13]. The intrinsic laboratory data of N<sub>2</sub>O catalytic decomposition over K-  
33 promoted Co-Mn-Al mixed oxide grains prepared by thermal treatment of LDH was used for  
34 model of pilot reactor for abatement of N<sub>2</sub>O emissions in off-gases from HNO<sub>3</sub> production.  
35 Pseudo-homogeneous one-dimensional model of an ideal plug flow reactor was used for reactor  
36 design [14].

37 In the presented paper, a developed model is being verified, attention will be focused on  
38 determination of effective diffusion coefficient and evaluation of mass transfer coefficient effect  
39 on N<sub>2</sub>O conversion. Pellets of Co-Mn-Al mixed oxide were prepared, tested for N<sub>2</sub>O  
40 decomposition in an inert gas and the obtained experimental data will be compared with the  
41 calculated N<sub>2</sub>O conversions based on kinetic data over catalyst grains in kinetic regime. The  
42 catalytic reactor for N<sub>2</sub>O abatement situated downstream the DeNO<sub>x</sub> technology (low NO<sub>x</sub>  
43 concentration) in nitric acid production unit will be estimated from laboratory data of N<sub>2</sub>O  
44 decomposition in simulated off gas over Co-Mn-Al mixed oxide pellets.

45

## 46 **2. Experimental**

47 The Co-Mn-Al (Co:Mn:Al molar ratio of 4:1:1) mixed oxide catalyst was prepared by  
48 calcination (500 °C) of coprecipitated LDH precursor [10]. Five batches were prepared  
49 altogether. Four batches were crushed, sieved, marked as Grain-1, Grain-2, Grain-3 and Grain-4  
50 and fraction 0.16 – 0.315 mm was used for the catalytic measurements. The catalysts were  
51 characterized in our previous publications [10, 12, 13]. As a fifth batch of the catalyst, we used  
52 the pellets (2.7x1.8 mm) prepared by pelletizing of the coprecipitated LDH precursor under such

53 pressure in order sufficient mechanical strength was achieved (30 MPa). The pellets, calcined 4 h  
 54 at 500 °C, were marked as Pellets .

55 The grained catalysts were tested in an integral fixed bed reactor R1. N<sub>2</sub>O catalytic  
 56 decomposition was performed at 300 – 450 °C and 100 – 265 kPa. Inlet gas contained 0.1  
 57 molar% N<sub>2</sub>O in He and space velocity 20 000 – 60 000 l kg<sup>-1</sup> h<sup>-1</sup> was applied.

58 The catalyst pellets were tested in an integral fixed bed reactor R2. N<sub>2</sub>O catalytic  
 59 decomposition was performed at atmospheric pressure, in temperature range of 240 – 450 °C and  
 60 space velocity of 6 530 l kg<sup>-1</sup> h<sup>-1</sup>. Inlet gas contained 0.1 molar% N<sub>2</sub>O in N<sub>2</sub>, but gas composition  
 61 simulating real waste gas from HNO<sub>3</sub> production downstream the DeNO<sub>x</sub> (0.1 molar% N<sub>2</sub>O,  
 62 0.01 molar% NO, 0.01 molar% NO<sub>2</sub>, 3 molar% H<sub>2</sub>O, 5 molar% O<sub>2</sub>) was also applied.

63 A care was taken to ensure sufficient approach to plug flow conditions in both R1 and R2  
 64 reactors. It is supposed that a rectangular velocity profile can be considered [15-17] for ratio:

$$65 \quad \frac{D_t}{d_p} > 10 \text{ to } 15 \quad (1)$$

66 Axial dispersion is negligible [15-17] for:

$$67 \quad \frac{L_b}{d_p} > \frac{a}{Pe_p} \ln\left(\frac{1}{1-X_A}\right), \text{ where } a = 8 \text{ or } 20 \quad (2)$$

68 Description of both reactors and verification of validity of conditions (1) and (2) are summarized  
 69 in Table 1. Both reactors can be considered as isothermal due to the low N<sub>2</sub>O concentration  
 70 leading to maximal adiabatic temperature rise of 4 °C. From the same reason, the absence of  
 71 internal and external heat transport limitations is supposed [18]. The criterions for 0.95%  
 72 avoiding the external (3) and internal (4) diffusion limitations [16] were confirmed for all  
 73 experimental runs in the R1 and R2 reactors.

$$74 \quad \text{Mears : } \frac{-r_A \cdot \rho_c \cdot r_p \cdot n}{k_c \cdot C_{Ab}} < 0.15 \quad (3)$$

75 Weisz-Prater : 
$$\frac{-r_A \cdot \rho_c \cdot L^2}{D_{eff} \cdot c_{As}} < 0.15 \frac{2}{n+1} \quad (4)$$

76

77 **3. Mathematical model**

78 Pseudo-homogeneous one-dimensional model of an ideal plug flow reactor in an  
79 isothermal regime mentioned in our previous paper [14] was used for modeling of the reactors.

80 The effect of internal and external mass transport was described by overall effectiveness factor  
81  $\Omega$ , which was incorporated into the 1<sup>st</sup> order kinetic equation  $-r_A = \Omega k c_A$ . In this paper, details  
82 of determinations of effective diffusion and mass transfer coefficients are described only.

83 The effective diffusion coefficient  $D_{eff}$  is dependent on morphology of porous catalyst:

84 
$$D_{eff} = \frac{\varepsilon_p}{q} \bar{D} \quad (5)$$

85 The  $\varepsilon_p/q$  ratio between 0.05 – 0.1 was published previously [16]. For the determination of the  
86 overall diffusivity of N<sub>2</sub>O in a multicomponent mixture ( $\bar{D}$ ), the contributions of molecular ( $D_{ij}$ )  
87 and Knudsen ( $D_{k,N_2O}$ ) diffusivity was considered together with stoichiometry of the reaction [15]:

88 
$$\frac{1}{\bar{D}} = \frac{1}{D_{k,N_2O}} + \frac{x_{N_2O} + x_{N_2O}}{D_{N_2O/N_2}} + \frac{0.5 \cdot x_{N_2O} + 0.5 \cdot x_{N_2O}}{D_{N_2O/O_2}} + \sum_{j=1}^n \frac{x_{N_2O}}{D_{N_2O/j}} \quad (6)$$

89 where  $j$  is component of gas mixture. The Knudsen diffusivity  $D_{k,N_2O}$  for pore with radius  $r_o$  was  
90 determined [16] as:

91 
$$D_{k,N_2O} = 97 \cdot r_o \cdot \sqrt{\frac{T}{M_{N_2O}}} \quad (7)$$

92 Binary diffusion coefficients  $D_{ij}$  were calculated according to Fuller, Schettler and  
93 Giddings [19]:

$$D_{i/j} = \frac{10^{-2} \cdot T^{\frac{7}{4}} \cdot (M_j^{-1} + M_i^{-1})^{\frac{1}{2}}}{p \left[ \epsilon_{v,j}^{\frac{1}{3}} + \epsilon_{v,i}^{\frac{1}{3}} \right]^2} \quad (8)$$

where  $\epsilon_{v,N_2} = 17.9$ ,  $\epsilon_{v,N_2O} = 35.9$ ,  $\epsilon_{v,O_2} = 16.6$ ,  $\epsilon_{v,H_2O} = 12.7$ ,

$\epsilon_{v,H_2} = 2.88$ ,  $\epsilon_{v,H_2O} = 11.17$ .

Mass transfer coefficient was determined according to correlation of Wakao and Funazkri [20] recommended for fixed bed and  $3 < Re < 1000$ :

$$Sh = 2.0 + (Re)^{1/2} \cdot 1.1(Sc)^{1/3} \quad (12)$$

100

## 101 4. Results and discussion

102 Chemical composition and results of analysis of porous structure of the prepared catalysts  
103 used in catalytic performance modeling are summarized in Table 2.

104

### 105 4.1 N<sub>2</sub>O decomposition over grained Co-Mn-Al mixed oxide catalysts

106 Temperature dependencies of N<sub>2</sub>O conversion over grained Co-Mn-Al mixed oxide  
107 catalysts are shown in Fig. 1. The relative error of measured conversions (which includes  
108 reproducibility of catalyst preparation and reproducibility of kinetic measurements) increased  
109 with decreasing N<sub>2</sub>O conversion from 9% to 88%. Kinetic parameters, evaluated according to 1<sup>st</sup>  
110 order rate law by the integral method (Table 2), were used for model verification of the R1  
111 reactor (Table 3). As was required, internal ( $\eta$ ) and overall ( $\Omega$ ) effectiveness factors are close to  
112 value 1. Only at the highest reaction temperature of 450 °C, the reaction rate is hindered by  
113 internal diffusion, whereas at lower temperatures the measurements proceeded in kinetic regime  
114 as was confirmed by the values of Mears and Weisz-Prater numbers. Good description of the  
115 experimental data was achieved (Fig. 2).

116

## 117 **4.2 Influence of pressure on the rate of N<sub>2</sub>O catalytic decomposition**

118 Since HNO<sub>3</sub> plants are working at higher pressure, it is important to examine the  
119 influence of pressure on the N<sub>2</sub>O decomposition rate. The increase of pressure led to the  
120 considerably higher N<sub>2</sub>O conversions (Fig. 3) due to the increase of N<sub>2</sub>O partial pressure and  
121 consequent higher reaction rate. The change of pressure can also influence surface species  
122 concentrations. When the catalysts surface is covered only slightly, the pressure increase causes  
123 higher surface coverage. However, no changes in surface concentrations are observed in the case  
124 of saturated surface. The effect of pressure on surface coverage by O<sub>2</sub>, NO<sub>x</sub> and H<sub>2</sub>O will be the  
125 subject of our further research.

126 Higher pressure also lowers binary diffusion coefficients what follows from Eq. (8). The  
127 results of the calculated diffusion coefficients in the pressure range of 0.1 – 0.6 MPa are shown  
128 in Table 4. Only slight decrease of  $D_{ij}$  was observed in this pressure range, while  $\bar{D}$  remained  
129 constant and nearly the same as the value of  $D_{k,N_2O}$  indicating that Knudsen diffusion is still  
130 prevailing in the pores. Further increase of pressure will cause higher gas density leading to the  
131 higher frequency of mutual molecule collisions and then, molecule diffusion will become  
132 involved, too. Due to decrease in  $D_{ij}$ , when the pressure increases, the mass transfer coefficient  
133 increased.

134

## 135 **4.3 N<sub>2</sub>O decomposition over Co-Mn-Al mixed oxide pellets**

136 Effective diffusion coefficient is the most uncertain parameter of the presented model due  
137 to the unknown tortuosity and average value of pore size of catalyst particles. Value of  $\varepsilon_p/q$  in the  
138 range of 0.05 – 0.1 is mentioned in literature [16]. In our case  $D_{eff}$  determined as  $D_{ef} = 0.12 \bar{D}$   
139 fits the N<sub>2</sub>O conversion curves over pellets satisfactory (Fig. 4). Parameters calculated according  
140 to the model for N<sub>2</sub>O decomposition over catalyst pellets at temperature 450 °C are summarized  
141 in Table 3. From Fig. 4 we can see that values of N<sub>2</sub>O conversion below 300 °C obtained over

142 pellets are very close to those obtained for the Grain-2 catalyst in kinetic regime (black dot-and-  
143 dash line in Fig. 4). Influence of mass transport limitation appears at higher temperatures i.e. at  
144 higher reaction rate. The internal diffusion limitation influences the reaction rate at temperatures  
145 higher than 300 °C. According to the value of Mears criterion (Eq. 3), concentration gradients  
146 between the bulk gas phase and catalyst surface in the R2 reactor at temperatures higher than 360  
147 °C exist (Table 3). For the purpose of scale-up, the internal diffusion limitation in the pellets can  
148 be accounted to kinetic constant, which is considered as microscopic phenomenon. Nearly  
149 identical values of the internal and overall effectiveness factor (Table 3) indicate that the reaction  
150 rate in R2 reactor is hindered by internal diffusion only. The reason is the order of magnitude  
151 higher resistance to the internal mass transfer in comparison with the resistance towards external  
152 diffusions. The hindering effect of external mass transport is overlapped by the internal diffusion  
153 limitation in the pores of pellets, since the intrusion of the reaction mixture to porous structure is  
154 difficult. This is important fact, since we can use the kinetic data obtained over industrial catalyst  
155 particles in the R2 laboratory reactor directly for the design of a pilot unit.

156 Kinetic parameters evaluated according to 1<sup>st</sup> rate law from the data of N<sub>2</sub>O  
157 decomposition over pellets in an inert gas and in simulated waste gas are summarized in Table 2,  
158 the comparison of calculated and experimental data is shown in Fig. 2. It is evident that 1<sup>st</sup> order  
159 kinetic does not describe the conversions curves precisely. The reason of it can be the  
160 complicated temperature dependence of complex kinetic constant, which includes kinetic  
161 constant and effectiveness factor. The dependencies of N<sub>2</sub>O conversion on space-time for pilot  
162 unit designated for abatement of N<sub>2</sub>O emission from HNO<sub>3</sub> plant are shown in Fig. 5. For  
163 instance, 3 400 kg of Co-Mn-Al mixed oxide pellets (2.7 x 1.8 mm) are necessary for cleaning  
164 (90% N<sub>2</sub>O conversion) of 30 000 m<sup>3</sup>/h (420 °C, 0.6 MPa) leading to the catalyst bed height of  
165 1.7 m in the reactor with diameter of 1.7 m and the pressure drop of 276 kPa.

166

## 167 5. Conclusions

168 Recently developed pseudo-homogeneous one-dimensional model of a fixed bed reactor  
 169 was verified with N<sub>2</sub>O decomposition over Co-Mn-Al mixed oxide catalysts grains and pellets.  
 170 Higher working pressure had positive impact on the N<sub>2</sub>O decomposition rate. Therefore, the  
 171 suitable position of N<sub>2</sub>O decomposition reactor in HNO<sub>3</sub> plant is upstream the expansional  
 172 turbine. Kinetic data measured over the catalyst pellets and described by 1<sup>st</sup> order rate law can be  
 173 directly used for estimation of the catalytic unit for N<sub>2</sub>O abatement in HNO<sub>3</sub> plant.

174

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 178 Technologies“.

179

### 180 **Nomenclature**

181	$c_A$	Concentration of A	(mol m <sup>-3</sup> )
182	$c_{Ab}$	Concentration of A in bulk of gas	(mol m <sup>-3</sup> )
183	$c_{As}$	Concentration of A on the catalyst surface	(mol m <sup>-3</sup> )
184	$d_p$	Catalyst particle diameter	(m)
185	$\bar{D}$	Overall diffusivity	(m <sup>2</sup> s <sup>-1</sup> )
186	$D_a$	Axial dispersion coefficient	(m <sup>2</sup> s <sup>-1</sup> )
187	$D_{eff}$	Effective diffusion coefficient	(m <sup>2</sup> s <sup>-1</sup> )
188	$D_{i/j}$	Binary diffusion coefficient of molecular diffusivity	(m <sup>2</sup> s <sup>-1</sup> )
189	$D_{k,N_2O}$	Knudsen diffusivity	(m <sup>2</sup> s <sup>-1</sup> )
190	$D_t$	Reactor tube diameter	(m)
191	$E_a$	Activation energy	(J mol <sup>-1</sup> )
192	$k$	Kinetic constant, 1 <sup>st</sup> order rate law	(m <sup>3</sup> s <sup>-1</sup> kg <sup>-1</sup> )
193	$k_c$	Mass transfer coefficient	(m s <sup>-1</sup> )
194	$k_o$	Pre-exponential factor	(m <sup>3</sup> s <sup>-1</sup> kg <sup>-1</sup> )
195	$L$	Characteristic dimension of catalyst particle	(m)
196	$L_b$	Length of catalyst bed	(m)
197	$M_i$	Molar weight of $i$ compound	(g mol <sup>-1</sup> )
198	$n$	Reaction order	(-)



199	$p$	Pressure	(Pa)
200	$\Delta p$	Pressure drop	(Pa)
201	$Pe_p = \frac{v \cdot d_p}{D_a}$	Peclet number	(-)
202	$q$	Tortuosity	(-)
203	$-r_A$	Reaction rate of component A	(mol s <sup>-1</sup> g <sup>-1</sup> )
204	$r_o$	Catalyst pore radius	(m)
205	$r_p$	Catalyst particle radius	(m)
206	$Re = \frac{v \cdot d_p \cdot \rho}{\eta_g}$	Reynolds number	(-)
207	$S_{BET}$	Specific surface area	(m <sup>2</sup> g <sup>-1</sup> )
208	$Sc = \frac{\eta_g}{\rho \cdot D_{N_2O/j}}$	Schmidt number, $j$ is carrier gas	(-)
209	$Sh = \frac{k_c \cdot d_p}{D_{N_2O/j}}$	Sherwood number, $j$ is carrier gas	(-)
210	$T$	Thermodynamic temperature	(K)
211	$v$	Superficial velocity	(m s <sup>-1</sup> )
212	$w$	Weight of catalyst	(kg)
213	$x_{N_2O}$	Molar fraction of N <sub>2</sub> O	(-)
214	$X_A$	Conversion of component A	(-)
215			
216	Greek letters		
217	$\varepsilon_p$	Porosity of catalyst particle	(-)
218	$\eta$	Internal effectiveness factor	(-)
219	$\eta_g$	Dynamic viscosity	(Pa s)
220	$\rho$	Density of gas	(kg m <sup>-3</sup> )
221	$\rho_c$	Bulk density of catalyst	(kg m <sup>-3</sup> )
222	$\Omega$	Overall effectiveness factor	(-)
223	$(\Sigma V)$	Diffusion volume	(-)
224			

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263

264 **Table 1** Description of experimental reactors R1 and R2

Reactor	$D_t$ (mm)	Catalyst weight $w$ (g)	Catalyst size (mm)	Length of bed <sup>1)</sup> $L_b$ (mm)	$D_t/d_p$ <sup>2)</sup>	$L_b/d_p$ <sup>2)</sup>
R1	5	0.1000	spheres 0.160-0.315	20	16	63 (required minimal value 15-38) <sup>3)</sup>
R2	40	4.5940	pellets 2.7 x 1.8	150	15	55 (required minimal value 48-120) <sup>3)</sup>

265 <sup>1)</sup> Including inert particles with approximately same diameter, <sup>2)</sup> The biggest particles are considered for verification  
266 of plug flow, <sup>3)</sup> Calculated for 95% N<sub>2</sub>O conversion and  $Pe_p = 0.5$  valid for low  $Re$  [15]

267

268

269 **Table 2** Chemical composition, porous structure and kinetic parameters determined for 1<sup>st</sup> order  
 270 rate law from experiments of N<sub>2</sub>O decomposition

Catalyst	Molar ratio Co:Mn:Al	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$r_0$ (nm)	$\rho_c$ <sup>3)</sup> (kg m <sup>-3</sup> )	$E_a$ (J mol <sup>-1</sup> )	$\ln k_0$ (m <sup>3</sup> s <sup>-1</sup> g <sup>-1</sup> )
Grain-1	4 : 1.15 : 1.57	93	12.0 <sup>1)</sup>	880	114 908 <sup>4)</sup>	9.76 <sup>4)</sup>
Grain-2	4 : 1.39 : 1.58	98	n.d. <sup>6)</sup>	n.d. <sup>6)</sup>	106 985 <sup>4)</sup>	8.31 <sup>4)</sup>
Grain-3	4 : 1.29 : 1.56	92	n.d. <sup>6)</sup>	n.d. <sup>6)</sup>	97 290 <sup>4)</sup>	6.75 <sup>4)</sup>
Grain-4	4 : 1.05 : 1.05	93	12.0 <sup>1)</sup>	n.d. <sup>6)</sup>	109 421 <sup>4)</sup>	9.38 <sup>4)</sup>
Pellets	n.d. <sup>6)</sup>	115	14.8 <sup>2)</sup>	1 282	75 799 <sup>4)</sup> 116 521 <sup>5)</sup>	1.96 <sup>4)</sup> 7.53 <sup>5)</sup>

271 <sup>1)</sup> Average pore radius determined from desorption branch of N<sub>2</sub> adsorption isotherm, <sup>2)</sup> Average pore radius  
 272 determined from Hg porosimetry, <sup>3)</sup> Bulk density determined from Hg porosimetry, <sup>4)</sup> Inert gas, <sup>5)</sup> Waste gas,  
 273 <sup>6)</sup> Not determined.

274

275

276 **Table 3** Parameters calculated for N<sub>2</sub>O decomposition over catalyst Grain-1 and Pellets

277 Conditions: 0.1 molar% N<sub>2</sub>O in He (Grain-1) or in N<sub>2</sub> (Pellets) in laboratory reactor R1 and R2, respectively,

278 temperature 450 °C, 0.1 MPa

Catalyst	GHSV (h <sup>-1</sup> kg <sup>-1</sup> )	<i>v</i> (m/s)	Re (-)	$\bar{D}$ (m <sup>2</sup> /s)	$D_{N_2O/j}$ <sup>1)</sup> (m <sup>2</sup> /s)	$D_{eff}$ (m <sup>2</sup> /s)	$D_{k,N_2O}$ (m <sup>2</sup> /s)	$k_c$ (m/s)	$\eta$ (-)	$\Omega$ (-)	Mears (-)	Weisz-Prater (-)	$\Delta p$ (Pa)
Grain-1 <sup>2)</sup>	60 000	0.22	0.1	4.72·10 <sup>-6</sup>	2.36·10 <sup>-4</sup>	4.72·10 <sup>-7 3)</sup>	4.72·10 <sup>-6</sup>	2.35	0.92	0.92	0.003	0.252	4750
Pellets	6 530	0.02	0.7	5.80·10 <sup>-6</sup>	6.98·10 <sup>-5</sup>	6.96·10 <sup>-7 4)</sup>	5.80·10 <sup>-6</sup>	0.07	0.22	0.21	0.874	28	280

279 <sup>1)</sup> *j* = He for grains, *j* = N<sub>2</sub> for pellets, <sup>2)</sup> Average grain size, <sup>3)</sup>  $D_{eff} = 0.1 \bar{D}$ , <sup>4)</sup>  $D_{eff} = 0.12 \bar{D}$

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281

282 **Table 4** Influence of pressure on diffusion coefficients and mass transfer coefficient283 Conditions: 0.1 molar% N<sub>2</sub>O in He, GHSV = 60 000 l h<sup>-1</sup> kg<sup>-1</sup>, Grain-1, 360 °C

Pressure (MPa)	$D_{N_2O/He}$ (m <sup>2</sup> /s)	$D_{N_2O/O_2}$ (m <sup>2</sup> /s)	$D_{N_2O/N_2}$ (m <sup>2</sup> /s)	$D_{k,N_2O}$ (m <sup>2</sup> /s)	$\bar{D}$ (m <sup>2</sup> /s)	$D_{eff}^{1)}$ (m <sup>2</sup> /s)	$k_c$ (m/s)
0.1	$1.87 \cdot 10^{-4}$	$5.43 \cdot 10^{-5}$	$5.53 \cdot 10^{-5}$	$4.42 \cdot 10^{-6}$	$4.41 \cdot 10^{-6}$	$4.41 \cdot 10^{-7}$	0.19
0.6	$3.18 \cdot 10^{-5}$	$9.24 \cdot 10^{-6}$	$9.40 \cdot 10^{-6}$	$4.42 \cdot 10^{-6}$	$4.41 \cdot 10^{-6}$	$4.41 \cdot 10^{-7}$	0.32

284 <sup>1)</sup>  $D_{eff}$  calculated as  $D_{eff} = 0.1 \bar{D}$ 

285

286

287 **Figure captions**

288

289 **Fig. 1** Temperature dependence of N<sub>2</sub>O conversion over grained Co-Mn-Al mixed oxide  
290 catalysts at GHSV = 60 000 l kg<sup>-1</sup> h<sup>-1</sup> and atmospheric pressure.

291

292 **Fig. 2** Comparison of measured N<sub>2</sub>O conversions and conversion calculated according to 1<sup>st</sup>  
293 order kinetic equation evaluated from experimental data measured over grains (e.g. in kinetic  
294 regime) and over the pellets (e.g. including internal diffusion).

295

296 **Fig. 3** Dependence of N<sub>2</sub>O conversion on pressure over Grain-1 catalyst.

297 Conditions: 360°C, GHSV = 60 000 l kg<sup>-1</sup> h<sup>-1</sup>, 0.1 molar% N<sub>2</sub>O in He.

298

299 **Fig. 4** Dependence of N<sub>2</sub>O conversion over the pellets on the effective diffusion coefficient at  
300 temperatures 240 – 450 °C.

301 Conditions: GHSV = 6 530 l kg<sup>-1</sup> h<sup>-1</sup>, 0.1 molar% N<sub>2</sub>O in N<sub>2</sub>, 0.1 MPa, kinetic parameters obtained over Grain-2  
302 and  $-r_A = \Omega k c_A$  was used for N<sub>2</sub>O decomposition modeling.

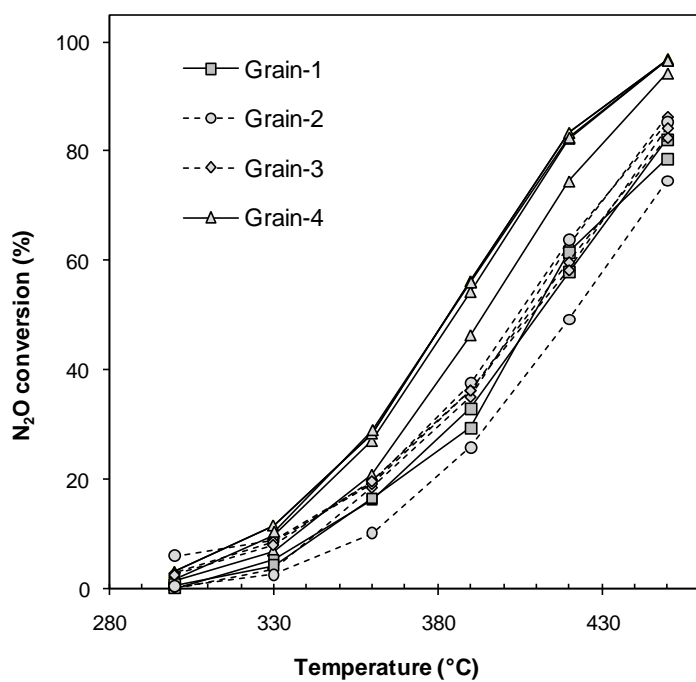
303

304 **Fig. 5** Dependence of calculated N<sub>2</sub>O conversion on space time in pilot reactor for N<sub>2</sub>O  
305 decomposition in waste gas from HNO<sub>3</sub> plant.

306 Conditions: inlet pressure 0.6 MPa,  $D_t = 1.7$  m,  $v = 0.62$  m s<sup>-1</sup>, kinetic equation  $-r_A = \exp\left(\frac{-116521}{RT} + 7.53\right)$ .

307

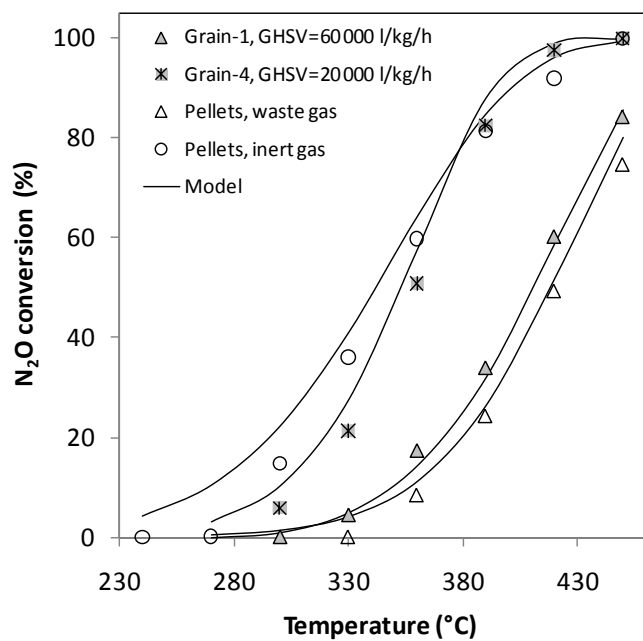




308

309 **Fig. 1**

310

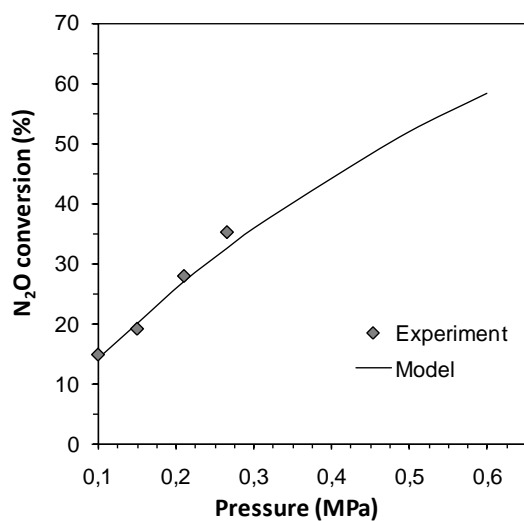


311

312 **Fig. 2**

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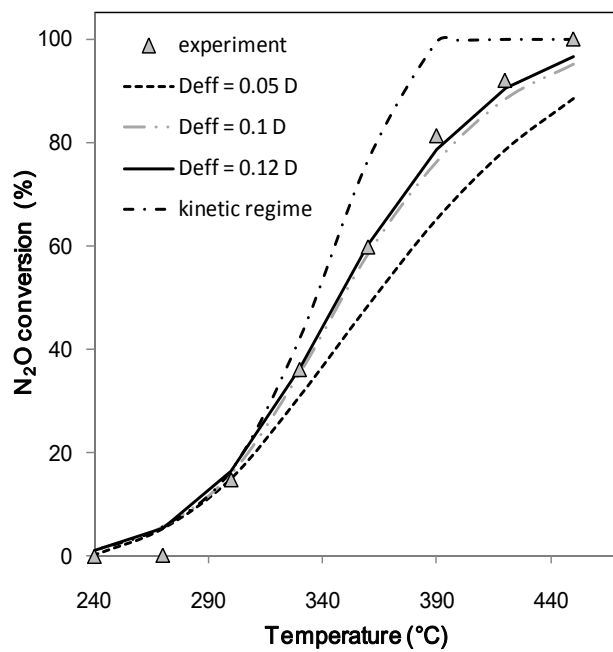


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316 **Fig. 3**

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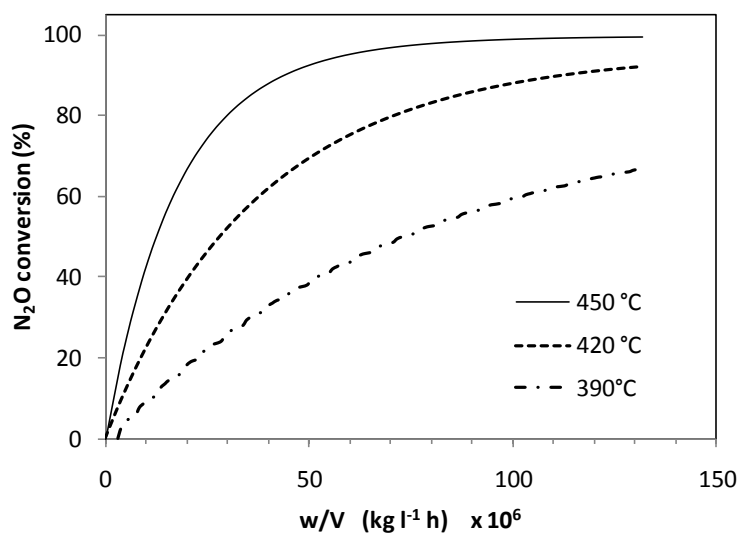
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320

321 **Fig. 4**

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324

325 **Fig. 5**

326