Simulation of N₂O Abatement in Waste Gases by Its Decomposition over a K-Promoted Co-Mn-Al Mixed Oxide Catalyst

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Abstract: Intrinsic data of N₂O catalytic decomposition over a K-promoted Co-Mn-Al mixed oxide prepared by the thermal treatment of a layered double hydroxide was used for the design of a pilot reactor for the abatement of N₂O emissions from the off-gases in HNO₃ production. A pseudo-homogeneous one-dimensional model of an ideal plug flow reactor under an isothermal regime (450 °C) was used for reactor design. A catalyst particle diameter of 3 mm is a compromise size because increasing the size of the catalyst particle leads to a decrease in the reaction rate because of an internal diffusion limitation, and particles with a smaller diameter cause a large pressure drop. A catalyst bed of 11.5 m³ was estimated for the target N₂O conversion of 90% upon the treatment of 30000 m³/h of exhaust gas (0.1 mol% N₂O, 0.005 mol% NO, 0.9 mol% H₂O, 5 mol% O₂) at 450 °C and 130 kPa.

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The catalytic decomposition of N₂O as a method to lower N₂O emissions in waste gases has recently attracted an increasing amount of attention because of the expected inclusion of N₂O in the greenhouse gas trade. Nitric acid plants have been found to be the largest industrial source of anthropogenic N₂O emissions (worldwide 400 kt N₂O per year) [1]. Several options are available for N₂O catalytic decomposition such as: (i) high-temperature catalytic decomposition immediately downstream of the ammonia burner, (ii) low-temperature N₂O catalytic decomposition upstream of the tail-gas expander and the NO_x emission reduction technology (DeNO_x), and (iii) low-temperature N₂O catalytic decomposition downstream of the DeNO_x process.

In this study, we concentrated on the low-temperature (≤ 450 °C) N₂O catalytic decomposition. There is still a problem to find a catalyst with sufficient activity and stability under real off-gas conditions because of water, oxygen, and NO_x inhibition effects [2]. Multicomponent mixed oxides that are prepared by the thermal treatment of layered double hydroxide (LDH) precursors seem to be good catalyst candidates for this reaction [3–5]. This contribution summarizes an estimation of N₂O abatement when using a catalytic reactor situated downstream of the DeNO_x technology in a

nitric acid production unit. Intrinsic kinetic data that was obtained from a laboratory experiment concerned with N₂O decomposition over a K-promoted Co-Mn-Al mixed oxide was used for reactor modeling.

1 Experimental

1.1 Catalyst preparation and N₂O decomposition

The Co-Mn-Al (Co:Mn:Al molar ratio of 4:1:1) mixed oxide catalyst containing 1.8 wt% K was prepared by the calcination (500 °C) of a coprecipitated LDH precursor. The method of preparation and the characterization of this catalyst have been described in our previous report [4].

N₂O catalytic decomposition was performed in an integral fixed-bed reactor (internal diameter of 5 mm) at 300–450 °C and 100–265 kPa with a catalyst grain of 0.16–0.315 mm. The gas composition simulated a real waste gas from HNO₃ production (0.1 mol% N₂O, 0.005 mol% NO, 0.9 mol% H₂O, 5 mol% O₂) and a space velocity of 20–60 L/(g·h) was used. Care was taken to avoid interference with physical transport phenomena.

The absence of mass transport limitations was confirmed by experiments and by satisfying the four dimensionless

criteria published by Kapteijn et al. [6]. Furthermore, a flat velocity profile and a negligible axial dispersion can be assumed because $d/d_p \approx 40$ and $L/d_p \approx 100$ [6], and this justifies using an ideal plug flow reactor to analyze the conversion data.

1.2 Mathematic model

A pseudo-homogeneous one-dimensional model of an ideal plug flow reactor in an isothermal regime (450 °C) was used for the reactor design (Eqs. (1)–(5)). The influence of internal and external diffusion is described by the overall effectiveness factor (Eqs. (6)–(13)) [7,8]. The influence of external heat transfer on the reaction rate was neglected and the catalyst particle was assumed to be isothermal under the given conditions. The first-order rate law was applied to the kinetics of N₂O decomposition [9].

Material balance of component A (A = N₂O) in the differential dimension dz:

$$\dot{n}_A^0 \frac{dX_A}{dz} = -r_A \cdot P \cdot \rho_b \quad (1)$$

Kinetic equation including the internal and external mass transfer limitations described by the overall effectiveness factor Ω :

$$-r_A = \Omega \cdot k_0 \cdot e^{\frac{-E_a}{RT}} \cdot c_A \quad (2)$$

Concentration of component A using the conversion X_A and neglecting the change of volumetric flow along the reactor because of the low N₂O concentration:

$$c_A = c_{A0} (1 - X_A) \left(\frac{p}{p_0} \right) \quad (3)$$

Pressure drop in the fixed bed:

$$-\frac{dp}{dz} = \frac{2 \cdot c_D \cdot \rho \cdot v^2}{d_p} \quad (4)$$

where c_D is the resistance coefficient according to the Ergun equation:

$$c_D = \frac{(1-\varepsilon)}{\varepsilon} \left[\frac{150 \cdot (1-\varepsilon)}{\text{Re}} + 1.75 \right] \quad (5)$$

The overall effectiveness factor Ω is defined by Eq. (6), where $1/\eta$ corresponds to the internal mass transport resistance and Φ_{gen}^2/Bi_M to the external mass transport resistance.

$$\frac{1}{\Omega} = \frac{1}{\eta} + \frac{\Phi_{\text{gen}}^2}{Bi_M} \quad (6)$$

$$\text{where } Bi_M = \frac{k_c}{D_{\text{eff}} \cdot a_v}, \quad a_v = \frac{4 \cdot \pi \cdot r_p^2}{4/3 \cdot \pi \cdot r_p^3} \quad (7)$$

To estimate the internal effectiveness factor η of catalyst particles with different shapes Eqs. (8)–(10) were used [10].

$$\eta = \frac{1}{\Phi_{\text{gen}}} \cdot \tanh \Phi_{\text{gen}} \quad \text{for } \Phi_{\text{gen}} < 4 \quad (8)$$

$$\eta = \frac{1}{\Phi_{\text{gen}}} \quad \text{for } \Phi_{\text{gen}} > 4 \quad (9)$$

where the generalized Thiele modulus Φ_{gen} is defined as:

$$\Phi_{\text{gen}} = \frac{V}{S} \cdot \sqrt{\frac{k \cdot \rho_c}{D_{\text{eff}}}}$$

$$\frac{V}{S} = \frac{d_p}{6} \quad \text{for sphere and cylinder } (L = d_p) \text{ particles,}$$

$$\frac{V}{S} = \frac{d_p}{5} \quad \text{for cylinder particles } (L = 2d_p), \quad \frac{V}{S} = \frac{d_p}{16} \quad \text{for}$$

$$\text{Raschig rings } (L = d_p), \quad \frac{V}{S} = \frac{d_p}{9} \quad \text{for Raschig rings } (L = 2d_p)$$

$$[10] \quad (10)$$

The N₂O effective diffusion coefficient D_{eff} is dependent on the morphology of the porous catalyst according to Eq. (11):

$$D_{\text{eff}} = \frac{\varepsilon_p}{q} \bar{D} \quad (11)$$

A ε_p/q ratio between 0.05–0.1 was reported in [6]. For the determination of the overall diffusivity of N₂O in a multi-component mixture (D) (Eq. (12)), the contribution of molecular (D_{ij}) and Knudsen (D_{k,N_2O}) diffusivity were considered together with the stoichiometry of reaction [11].

$$\frac{1}{D} = \frac{1}{D_{k,N_2O}} + \frac{10^{-3} + 10^{-3}}{D_{N_2O/N_2}} + \frac{0.5 \times 10^{-3} + 0.5 \times 10^{-3}}{D_{N_2O/O_2}} + \frac{10^{-3}}{D_{N_2O/N_2}} + \frac{10^{-3}}{D_{N_2O/O_2}} + \frac{10^{-3}}{D_{N_2O/H_2O}} \quad (12)$$

The Knudsen diffusivity D_{k,N_2O} for a pore with radius r_0 is determined [6] as:

$$D_{k,N_2O} = 97 \cdot r_0 \cdot \sqrt{\frac{T}{M_{N_2O}}} \quad (13)$$

Binary diffusion coefficients D_{ij} were calculated using the Fuller, Shettler, and Giddings equations [12].

2 Results and discussion

A comparison of the temperature dependence of N₂O conversion over a K-promoted Co-Mn-Al mixed oxide as measured in an inert gas and with a simulated off-gas over a powder catalyst is shown in Fig. 1.

An increase in reactor pressure from atmospheric pressure to 200 kPa led to an order of magnitude increase in N₂O conversion (not shown). The K content was chosen according to our previous results [4,5]. We found an optimal content for the K promoter corresponding to the highest conversion in the presence of O₂, H₂O, and NO_x.

Fig. 1. Temperature dependence of N_2O conversion in inert and simulated waste gas. Waste gas: SV = 20 L/(g·h), 0.1 mol% N_2O , 0.005 mol% NO, 0.9 mol% H_2O , 5 mol% O_2 , rest He; Inert gas: SV = 20 L/(g·h), 0.1 mol% N_2O , rest He.

The kinetic parameters for the 1st rate law were evaluated by an integral method of the laboratory data and this was used for an estimation of the pilot reactor to lower the N_2O emissions during HNO_3 production. The textural characterization of the Co-Mn-Al mixed oxide catalyst that was pelletized at 6 MPa, and published in our recent work [13] was also used. Figure 2 shows the mesopore size distribution that was determined by the BJH method from the physical desorption of nitrogen. A well resolved maximum was located at 9 nm and a diffuse and not very distinct maximum at about 2 nm.

Fig. 2. Mesopore distribution obtained from the physical desorption of nitrogen over the Co-Mn-Al mixed oxide pelletized at 6 MPa [13].

An example of the effective diffusion coefficient (D_{eff}) calculation, according to Eqs. (11)–(13), for the highest catalyst pore radius of 9 nm is shown in Table 1. The contribution of molecular diffusion (D_{ij}) to the overall N_2O diffusivity ($\bar{D}$) can be evidently ignored because of the low N_2O concentration in the model off-gas and, therefore, Knudsen diffusion prevails in the pores.

The effective diffusion coefficient N_2O (D_{eff}) is determined only by the dimension of the pore radius and it can be considered independent of the gas composition and

Table 1 The calculated diffusion coefficients at $T = 723 \text{ K}$, $p = 0.1 \text{ MPa}$, model gas (0.1 mol% N_2O , 5 mol% O_2 , 2 mol% H_2O , rest N_2), and a pore radius of 9 nm

$D_{\text{k},\text{N}_2\text{O}}$	$D_{\text{N}_2\text{O}/\text{N}_2}$	$D_{\text{N}_2\text{O}/\text{O}_2}$	$D_{\text{N}_2\text{O}/\text{H}_2\text{O}}$	$\bar{D}$	D_{eff}^a
(m^2/s)	(m^2/s)	(m^2/s)	(m^2/s)	(m^2/s)	(m^2/s)
3.54×10^{-6}	0.697×10^{-4}	0.268×10^{-4}	0.348×10^{-4}	3.54×10^{-6}	1.77×10^{-7}

^aCalculated as $D_{\text{eff}} = 0.05 \bar{D}$.

pressure under the given conditions. The effect of catalyst pore size on internal and external diffusion is expressed as a dependence of the internal (η) and external effectiveness factor (Bi_M/Φ_{gen}^2) on the catalyst pore radius, as shown in Fig. 3. As expected, both the internal and external effectiveness factors increased with an increase in pore size. However, the values for the external effectiveness factor are one order of magnitude higher than the values for the internal effectiveness factor leading to the conclusion that the N_2O decomposition under the conditions examined is hindered by internal diffusion in the catalyst pores.

Figure 4 shows the dependence of the internal effectiveness factor η on the catalyst particle size for the different

Fig. 3. Dependence of the internal and external effectiveness factors on the catalyst pore radius. Calculated for the inlet parameters mentioned in Table 2 and a N_2O conversion of 90%.

Fig. 4 Dependence of the internal effectiveness factor on the catalyst particle size. Calculated for simulated waste gas containing 0.1 mol% N_2O , 0.005 mol% NO, 0.9 mol% H_2O , 5 mol% O_2 .

catalyst shapes, calculated according to Eqs. (8)–(10). A sharp decrease in η with an increase in d_p was observed. For the catalyst particles with diameters larger than 3 mm, the overall reaction rate is significantly limited by diffusion in pores, as is evident from the low values of the internal effectiveness factor. A higher value at a given particle diameter was calculated for the particle shapes with a higher volume/external surface ratio.

The dependence of the pressure drop on the catalyst particle diameter for the different catalyst shapes is shown in Fig. 5. The pressure drop increases with a lowering of the particle size (leading to an increase in the internal effectiveness factor) and it is also dependent on particle shape.

The lowest pressure drop was calculated for the Raschig rings. It is clear that the choice of the catalyst particle size is always a compromise because increasing the size of the catalyst particle leads to a decrease in the reaction rate because of the internal diffusion limitation whereas particles with a smaller diameter cause a large pressure drop.

For the N₂O emissions abatement reactor design, we chose extrudates of 3 mm × 3 mm in dimension. The inlet and calculated parameters are given in Table 2. For the reactor tube with a diameter of 3.5 m, a catalyst bed of

Fig. 5 Dependence of the pressure drop on the particle diameter for the different catalyst shapes. The pressure drop was calculated for a superficial velocity of 1.6 m/s and $\varepsilon = 0.33$ (sphere), 0.38 (extrudate), 0.51 (Raschig ring) [14].

11.5 m³ is necessary for a N₂O conversion of 90%. The overall reaction rate was limited by internal diffusion as is evident from the low value of the internal effectiveness factor.

Table 2 Inlet and calculated parameters for N₂O abatement in simulated waste gas from HNO₃ production

Input parameters		Calculated parameters	
Volume flow (NTP)	30 000 m ³ /h	N ₂ O effective diffusion coefficient	1.77×10 ⁻⁷ m ² /s
Temperature	450 °C	Kinetic constant (450 °C)	2.88×10 ⁻⁵ m ³ /(s·g)
N ₂ O concentration	0.1 mol%	Mass transfer coefficient	0.04 m/s
Pressure	130 kPa	Internal effectiveness factor	0.11
Porosity of catalyst bed	0.38	Overall effectiveness factor	0.10
Specific surface area	93 m ² /g	Catalyst bed volume ^b	11.5 m ³
Average pore radius	9 × 10 ⁻⁹ m	Catalyst weight ^b	1.5×10 ⁴ kg
Equivalent particle diameter ^a	0.0037 m	Pressure drop ^b	2.0×10 ⁴ Pa
Bulk catalyst density	2081 kg/m ³		

^aExtrudate 3×3 mm. ^bCalculated for the target 90% N₂O conversion.

Concentration profile in the spherical catalyst particles ($d_p = 3$ mm) was calculated according to Eq. (14) [8], valid for the 1st order rate law. Concentration profile is shown in Fig. 6. Because of slow diffusion in catalyst pores, the N₂O catalytic decomposition reaction proceeds only in an external shell while the particle core remains almost unused. For this reason, our future efforts will focus on the preparation of supported catalysts in order to not have expensive transition metals in the whole catalyst volume. Furthermore, the larger pores will be useful for the increase of diffusion rate.

$$\frac{c_A}{c_{As}} = \frac{r}{r_p} \cdot \left(\frac{\sinh \Phi_{\text{gen}} \cdot r / r_p}{\sinh \Phi_{\text{gen}}} \right) \quad (14)$$

The relatively high catalyst weight of 1.5×10^4 kg can be decreased by the suitable positioning of the catalytic N₂O abatement reactor upstream of an expansion turbine because

higher pressure accelerates the reaction rate. However, pre-heating will be necessary because of the low gas temperature.

Fig. 6 Concentration profile in a sphere catalyst particle with a diameter of 3 mm.

3 Conclusions

Intrinsic laboratory data of the N_2O catalytic decomposition over a K-promoted Co-Mn-Al mixed oxide was used to design a pilot reactor for the abatement of N_2O emissions in off-gases from HNO_3 production. A catalyst bed of 11.5 m^3 was estimated for a target N_2O conversion of 90% for the treatment of $30000 \text{ m}^3/\text{h}$ of exhaust gas (0.1 mol% N_2O , 0.005 mol% NO , 0.9 mol% H_2O , 5 mol% O_2) at 450°C and 130 kPa. The reaction is hindered by internal diffusion in the catalyst pores as is evident from the obtained internal effectiveness factor. The optimization of the size and shape of the catalyst particles with the aim of decreasing the effect of internal mass transport at an acceptable pressure drop is still of interest.

Nomenclature

A	Component A
a_v	Surface of 1 m^3 of the catalyst (m^2/m^3)
Bi_M	Biot number
c_A	Concentration of A (mol/m^3)
c_{As}	Concentration of A on the external surface of the catalyst particle (mol/m^3)
c_{A0}	Concentration of compound A at the reactor inlet (mol/m^3)
c_D	Resistance coefficient
d_p	Catalyst particle diameter (m)
d_t	Reactor diameter (m)
$\bar{D}$	Overall diffusivity (m^2/s)
D_{ij}	Binary diffusion coefficients of molecular diffusivity (m^2/s)
$D_{k,\text{N}_2\text{O}}$	Knudsen diffusivity (m^2/s)
D_{eff}	Effective diffusion coefficient (m^2/s)
E_a	Activation energy (J/mol)
k	Kinetic constant ($\text{m}^3/(\text{s}\cdot\text{kg})$)
k_o	Pre-exponential factor ($\text{m}^3/(\text{s}\cdot\text{kg})$)
k_c	Mass transfer coefficient (m/s)
L	Length of catalyst bed (m)
$M_{\text{N}_2\text{O}}$	Molar weight of N_2O (g/mol)
$\dot{n}_A^0$	Molar flow of A at the inlet (mol/s)
P	Reactor cross section (m^2)
p	Pressure (Pa)
p_0	Total pressure at the reactor inlet (Pa)
q	Tortuosity
r	Distance from the center of the spherical catalyst particle (m)
$-r_A$	Reaction rate of component A ($\text{mol}/(\text{s}\cdot\text{g})$)
r_o	Catalyst pore radius (m)
r_p	Catalyst particle radius (m)

R	Universal gas constant (J/(mol·K))
Re	Reynolds number
S	External surface area of catalyst particle (m^2)
SV	Space velocity (L/(g·h))
T	Thermodynamic temperature (K)
V	Catalyst particle volume (m^3)
v	Superficial velocity (m/s)
X_A	Conversion of component A
z	Distance from the inlet of the bed (m)

Greek letters

ε	Porosity of the catalyst bed
ε_p	Porosity of catalyst particle
η	Internal effectiveness factor
π	Ludolph number
ρ	Density of gas (kg/m^3)
ρ_c	Bulk density of catalyst (kg/m^3)
ρ_b	Density of catalyst bed (kg/m^3)
Φ_{gen}	Generalized Thiele modulus
Ω	Overall effectiveness factor

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