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New catalyst for removal of N₂O from nitric acid plant tail gases

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1. Introduction

Nitrous oxide is formed as an undesirable by-product during catalytic oxidation of ammonia in nitric acid production plants. Taking into account the global production of the nitric acid and the high global warming potential of N₂O, much emphasis is currently placed on the development of methods for N₂O emissions abatement. Among them, N₂O catalytic decomposition to oxygen and nitrogen is the simplest one (Eq. 1). The high temperature catalytic decomposition (at about 850 °C) situated immediately downstream of the ammonia burner and the “end-of-pipe” low temperature (at about 450°C) N₂O catalytic decomposition are considered there.



Our research has been focused on development of a catalyst for the low temperature N₂O catalytic decomposition. The resistance against water and oxygen inhibition, high performance in the presence of NO_x (NO+NO₂) and long-term stability in wet acidic environment are crucial requirements for this catalyst.

From a big group of catalysts reported for this process, the cobalt-containing mixed oxides prepared from layered double hydroxide (LDH) precursors have been found to be very efficient in N₂O decomposition [1-6]. Layered double hydroxides (also called hydrotalcite-like compounds or hydrotalcites) are layered materials consisting of positively charged hydroxide layers separated by interlayers composed of anions and water molecules. The chemical composition of LDHs can be expressed by general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}\text{yH}_2\text{O}]^x$ where M^{II} and M^{III} are divalent and trivalent metal cations, Aⁿ⁻ is an n-valent anion, and x usually has values between 0.20 and 0.33. After heating at moderate temperatures, LDHs give finely dispersed mixed oxides of M^{II} and M^{III} metals with high surface area and good thermal stability. We have tested different combinations of metal cations in hydroxide layers at constant M^{II}/M^{III} molar ratio of 2 (M^{II}=Co, Ni, Cu, Mg; M^{III}=Al, Mn, Fe; Aⁿ⁻=CO₃²⁻) [7-8]. Optimization of chemical composition resulted in obtaining the LDH-related Co-Mn-Al mixed oxide with Co:Mn:Al molar ratio of 4:1:1, which showed high activity and stability in wet gas containing oxygen and NO_x [9].

The improvement of catalytic activity of cobalt-containing mixed oxides by their modification with potassium promoter was reported [10-13]. Our recent results showed that the optimum content of potassium in Co-Mn-Al mixed oxide is 0.9-1.6 wt% K [12, 14]. It was shown that the beneficial effect of K is mainly of electronic origin as it was found from direct correlation of the catalytic activity with the catalyst electron work function [15]. Models of catalytic reactor for N₂O abatement from waste gas from HNO₃ production plant

using intrinsic kinetic data over grains of Co-Mn-Al mixed oxide [16] and/or kinetic data obtained over laboratory prepared Co-Mn-Al mixed oxide tablets [17] were reported.

In the present work, the Co-Mn-Al mixed oxide modified by K was prepared in the pilot plant scale for the first time and tested in real conditions. Results of N₂O catalytic decomposition in the pilot plant reactor installed at the bypassed tail gas from the nitric production plant are shown and obtained kinetic data are used for modeling of full scale reactor for N₂O emissions abatement.

2. Experimental methods

2.1 Catalyst preparation and characterization

The Co-Mn-Al LDH precursor with Co:Mn:Al molar ratio of 4:1:1 was prepared by coprecipitation of corresponding nitrates in an alkaline Na₂CO₃/NaOH solution at 25 °C and pH 10. The resulting suspension was filtered off, washed with water, dried at 105 °C and calcined for 4 hours at 500 °C in air. The resulted mixed oxide was milled, impregnated with KNO₃, recalcined, formed into tablets 5 x 5 mm and denoted as K/Co₄MnAlO_x. The catalyst was produced by the ASTIN Catalysts and Chemicals company. Various methods, namely the chemical analysis (AAS), powder XRD, XPS, N₂ physisorption, He pycnometry, Hg porosimetry, and H₂-TPR were used for characterization of the fresh and used (i.e., after application in the pilot plant reactor) catalysts. The characterization methods are described in more details in [12].

2.2 N₂O catalytic decomposition

Pilot plant catalytic measurements of N₂O decomposition were performed in a fixed bed stainless steel reactor (0.31 m internal diameter) in the temperature range from 300 to 450 °C and inlet pressure of 0.6 MPa. Reactor was connected at the bypassed tail gas from the nitric production plant downstream the SCR NO_x/NH₃ catalyst. The catalyst (69.1 kg weight, 1361 kg m⁻³ bed density) was placed on a stainless steel grate and sieve. Then the bed was filled by ceramic spheres to the total high of 0.75 m. Feed to the reactor was varied between 300 and 600 kg h⁻¹ and contained typically 400-700 ppm N₂O together with oxygen, water vapor and low concentration of NO, NO₂ and NH₃. The infrared (N₂O, NO, NH₃) and chemiluminescence (NO, NO₂) on-line analyzers were used for analysis of the gas at the catalyst bed inlet and outlet. N₂O concentrations in steady state were used for determination of N₂O conversion. Reactor was equipped with on-line monitoring concentrations of all measured gas components, temperature in catalyst bed and pressure drop.

2.3 Reactor and kinetics models

Pseudo-homogeneous one-dimensional model of an ideal plug flow reactor in isothermal regime at steady state was used for the modeling of pilot plant fixed bed reactor (Eq. 2-5) [18]. The first-order rate law (Eq. 4) was supposed for the kinetics of N₂O decomposition in the excess of oxygen and constant concentration of water vapor and NO_x [19].

$$\text{Material balance of component A (A = N}_2\text{O): } \frac{dX_A}{dz} = r \frac{p^o \cdot M}{R \cdot T^o} \cdot \frac{A \cdot \rho_{bed}}{c_{A0} \cdot \dot{m}} \quad (2)$$

$$\text{Impulse balance: } -\frac{dp}{dz} = \frac{c_D \cdot \rho \cdot v^2}{d_{ekv}}, \quad c_D = \frac{(1-\varepsilon)}{\varepsilon^3} \left[\frac{368 \cdot (1-\varepsilon)}{Re} + 1.24 \right] \quad (3)$$

$$\text{Kinetic equation: } r = k \cdot c_A, \quad k = k_o \cdot e^{\frac{-E_a}{RT}} \quad (4)$$

$$\text{Stoichiometry: } c_A = c_{A0} (1 - X_A) \left(\frac{P}{P_0} \right) \quad (5)$$

This simple model was sufficient for pilot plant reactor description because (i) the change of volumetric flow along the reactor can be neglected due to the low N₂O concentration, (ii) temperature gradients in catalyst bed are not expected on account of a low heat release during the reaction, and (iii) axial diffusion was negligible as was proven by the Bodenstein number ($Bo=955 > 100$). Moreover, plug flow conditions and a homogeneous distribution of the gas residence time were validated because the criterion $L_{bed}/d_p > 100$ was met. The absence of a rate limitation by external mass transport was verified for temperatures lower than 400 °C by calculation of Mears criterion ($Mears < 0.15$) [18]. Polymath software was used for solving of system of ordinary differential equations (Eq. 2-5).

For the evaluation of kinetic parameters (k_o , E_a) from the measurements in the pilot plant reactor, only mass balance was considered while the impulse balance could be neglected because of the pressure drop lower than 10 kPa was measured [19]. Integrated form of mass balance was used for k calculation (Eq. 6), then k_o , E_a were determined from Arrhenius plot $\ln k^*$ versus $1/T$.

$$\ln \frac{1}{1 - X_A} = k^* \frac{w}{\dot{m}} \quad (6)$$

3. Results and discussion

3.1 Characterization of fresh and used catalyst

The potassium content in the catalyst as well as K/Co molar ratio determined by AAS corresponded well to the value adjusted in alkali nitrate solution during impregnation. Specific surface area of K/Co₄MnAlO_x tablets was comparable with that obtained with a grain catalyst prepared in laboratory conditions. Spinel-type mixed oxide was found in the K/Co₄MnAlO_x catalyst by XRD. In addition, graphite phase was present in the fresh catalyst and disappeared in the used one (not shown here). No substantial changes in chemical composition, textural characteristics, crystallinity and catalyst reducibility (expressed as hydrogen consumption determined from H₂-TPR) were observed after using the catalyst in the pilot plant reactor (Table 1).

Table 1 Chemical analysis, textural parameters and reducibility of the fresh and used K/Co₄MnAlO_x catalysts

Catalyst	AAS (wt%)				Molar ratio Co:Mn:Al	S_{BET} (m ² g ⁻¹)	ρ_{Hg} (g cm ⁻³)	ρ_{He} (g cm ⁻³)	R^1 (nm)	TPR ²⁾ (mmol/g)
	Co	Mn	Al	K						
Fresh	45.0	9.28	5.16	1.25	4 : 0.66 : 0.74	93	2.3	4.39	3.8	5.61
Used ³⁾	49.9	8.51	5.20	1.27	4 : 0.73 : 0.91	87	2.36	4.98	4.0	5.73

¹⁾ Average pore radius $R=2V/A$

²⁾ (25-500°C)

³⁾ For 112 days

Table 2 XPS analysis of the fresh and used K/Co₄MnAlO_x catalysts

Catalyst	XPS (mol%)						Molar ratio				
	Co	Mn	Al	K	O	C	Co:Mn:Al	K:Co	Co:Mn	Co:Al	Mn:Al
Fresh	18.14	3.34	8.68	1.71	54.13	13.99	4 : 0.7 : 1.9	0.094	5.43	2.09	0.38
Used ¹⁾	17.45	4.83	10.78	2.26	60.20	4.47	4 : 1.1 : 2.5	0.130	3.61	1.62	0.45

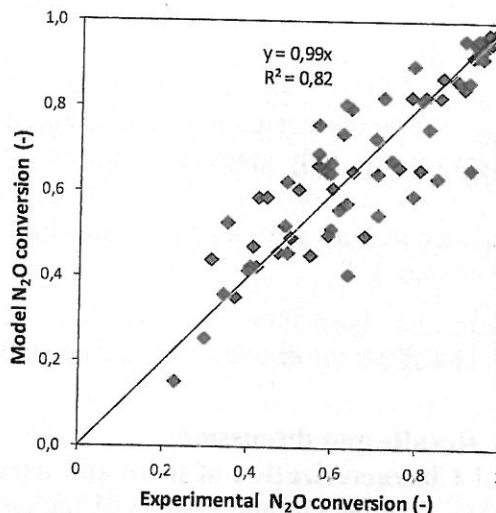
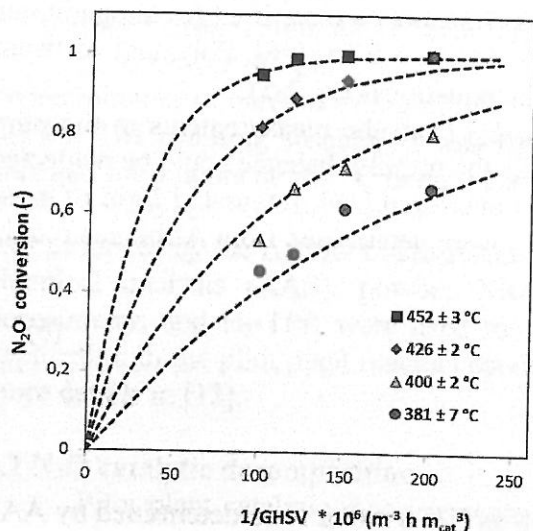
¹⁾ For 112 days

Co:Mn:Al molar ratios on the fresh catalyst surface calculated from XPS data (Table 2) showed significant surface enrichment by Al. Relation between bulk and surface K/Co molar ratio demonstrated that concentration of potassium on the surface is higher than in the bulk.

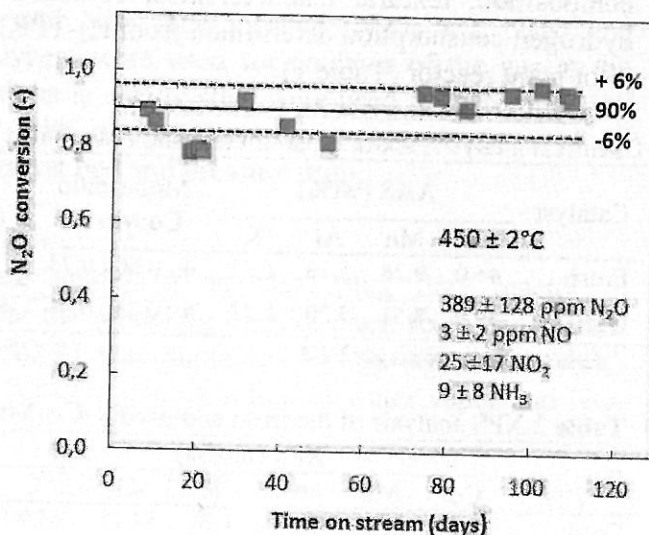
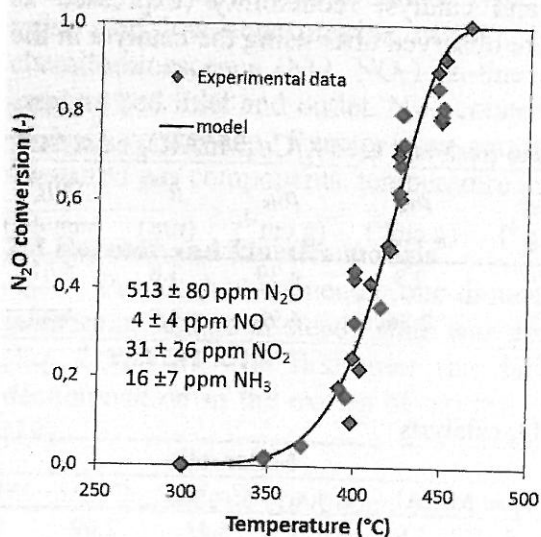
The enrichment of catalyst surface by Al and K is more evident after the catalytic testing. On the other hand, a decrease in the surface cobalt concentration was observed in used catalyst.

3.2 N₂O catalytic decomposition in pilot plant reactor

Results of kinetic experiment, when the inlet total gas flow was varied, are shown in Fig. 1. It can be concluded that N₂O catalytic decomposition is satisfactory described by the 1st order kinetic equation (Eq. 4) at given process conditions (Fig. 2) and values of $E_a = 97\,766 \pm 4554 \text{ J mol}^{-1}$ and $k_0 = 3.17 \cdot 10^8 \text{ h}^{-1}$ were determined.



Dependence of N₂O conversion on space time (points—experimental data, average values, line—model) on K/Co₄MnAlO_x catalyst (left) and comparison of experimental N₂O conversions with conversions calculated according to 1st order kinetics (right)
(512 ± 135 ppm N₂O, 26 ± 16 ppm NO_x, 9 ± 3 NH₃, p = 0.6 MPa, GHSV = 4975-9952 m³ m_{bed}⁻³ h⁻¹)



Temperature dependence of N₂O conversion (left) and stability test (right) over K/Co₄MnAlO_x catalyst in the pilot plant test (GHSV=8 620 m³ m_{bed}⁻³ h⁻¹, p=0.6 MPa)

Temperature dependence of N₂O conversion over K/Co₄MnAlO_x tablets is shown in Fig. 2. Scattering of N₂O conversion can be caused by variable composition of gas mixture at the reactor inlet. Our laboratory experiments performed in recent years demonstrated that N₂O

decomposition is inhibited by nitrogen oxides (NO and NO₂), oxygen (up to 3 mol% O₂, at higher content almost no effect was observed [17]) and water vapor [12]. Variation in NO_x concentration was observed during on-line NO_x analysis at the catalyst bed inlet, oxygen and water vapor contents were not measured. Long-term stability of K/Co₄MnAlO_x catalyst during the pilot plant testing is shown in Fig. 2. No deactivation was observed and N₂O conversion of 90 ± 6% at 450 °C was kept for 112 days.

3.3. Modeling of full scale reactor

Evaluated kinetic parameters determined from experiments over the catalyst tablets in the pilot plant reactor describe the reaction rate including internal diffusion hindering effect. At the assumption that these data are not influenced by macrokinetic phenomena of the pilot plant reactor, they were directly used for reactor scale-up. By simultaneous solving Eqs. 2-6, K/Co₄MnAlO_x catalyst amount of 3 155 kg was determined as necessary for 90% N₂O conversion (450°C, 0.6 MPa) in waste gas with total gas flow 30 000 m³/h (Table 3).

Table 3 Inlet and calculated parameters for N₂O abatement in waste gas from HNO₃ production

Inlet parameters		Calculated parameters	
Pressure	600 000 Pa	Catalyst weight ^a	3 155 kg
Temperature	450 °C	Catalyst bed volume	2.3 m ³
Volume flow	30 000 m ³ /h (NTP)	Pressure drop	10 kPa
N ₂ O concentration	0.07 mol%	Price of catalyst	360 500 Eu
Kinetic constant	27.4 h ⁻¹ (1 st order)	Price of N ₂ O disposal ^{b,c}	0.6 Eu/ 1 kg N ₂ O

^aCalculated for reactor diameter of 1.5 m and 90% N₂O conversion, ^bWithout energy, investment and profit costs calculated for catalyst lifetime of 2 years

4. Conclusions

The preparation of multicomponent K-doped Co-Mn-Al mixed oxide catalyst for low-temperature N₂O decomposition was successfully reproduced in pilot plant scale; the catalysts was formed into the tablets. In the pilot plant tests, high output in N₂O removal from the bypass tail gases from the nitric production plant was reached for 112 days without any deactivation. Obtained experimental data were evaluated by applying the 1st order kinetic equation and used for calculation of full-scale reactor parameters. Taking into account the experience with synthesis of K-doped Co-Mn-Al mixed oxide catalyst in pilot plant scale, price of 114 EUR per kg of catalyst can be supposed. Price of N₂O disposal at the assumption of catalyst lifetime of 2 years was determined as 0.6 EUR per 1 kg of decomposed N₂O.

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Nomenclature

A	Reactor cross section area	(m ²)
$Bo = \frac{Pe_{ax} \cdot L_{bed}}{d_p}$	Bodenstein number	(-)
c_A	Concentration of component A	(mol m ⁻³)
c_{A0}	Concentration of component A at the reactor inlet	(mol m ⁻³)
c_D	Resistance coefficient for Re/(1-ε)<500	(-)
d_p	Catalyst particle diameter	(m)
$d_{ekv} = 3 \cdot L_p \cdot d_p / (2 \cdot L_p + d_p)$	Equivalent catalyst particle diameter (cylinder)	(m)

E_a	Activation energy	(J mol ⁻¹)
k	Kinetic constant	(m ³ h ⁻¹ kg ⁻¹)
$k^* = k \frac{p^o M}{RT^o}$	Kinetic constant	(h ⁻¹)
k_o	Pre-exponential factor	(h ⁻¹)
L_{bed}	Height of catalyst bed	(m)
L_p	Catalyst particle height	(m)
M	Molar weight of waste gas	(kg mol ⁻¹)
$Mears = \frac{n \cdot \rho_{bed} \cdot d_p / 2}{k_c c_A} r$	Mears criterion	(-)
n	Reaction order	(-)
\dot{m}	Weight gas flow	(kg h ⁻¹)
p, p^o, p_0	Pressure, normal pressure, pressure at the reactor inlet	(Pa)
$Pe_{ax} = 1 / \left(\frac{3 \cdot 10^7}{Re^{2.1}} + \frac{1.35}{Re^{1.8}} \right)$	Peclet number	(-)
r	Reaction rate	(mol h ⁻¹ kg ⁻¹)
$Re = \frac{v \cdot d_p \cdot \rho}{\eta}$	Reynolds number	(-)
T, T^o	Thermodynamic temperature, normal temperature	(K)
v	Superficial velocity	(m s ⁻¹)
X_A	Conversion of component A	(-)
ε	Porosity of the catalyst bed	(-)
ρ	Density of gas	(kg m ⁻³)
ρ_{bed}	Density of catalyst bed	(kg m ⁻³)
η	Dynamic viscosity of waste gas	(Pa s)

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