

Alkali metals as promoters in Co-Mn-Al mixed oxide for N₂O decomposition

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Abstract

Alkali promoted Co₄MnAlO_x mixed oxide (molar ratio of alkali metal/Co = 0.037) were prepared by impregnation of calcined Co-Mn-Al hydrotalcite (molar ratio Co:Mn:Al = 4:1:1) with an aqueous solution of Li, Na, K, Rb or Cs nitrate. The catalysts were characterized by AAS, SEM/EDX, N₂ physisorption, XRPD, XPS, H₂-TPR, TPD of CO₂ and NH₃ and tested for N₂O decomposition in inert gas and simulated waste gas from HNO₃ production. N₂O conversion over alkali promoted Co₄MnAlO_x mixed oxide decreased in order Cs > Rb > K > Na = Co₄MnAlO_x > Li in inert gas and was shifted to the lower values in the presence of typical components (NO_x, O₂ and H₂O) of flue gas. The addition of alkali promoters to the Co₄MnAlO_x mixed oxide resulted in a modification of both electronic properties of active metals and acid-base function of the catalyst surface. The promotional effect of alkali metals is connected with their ionization potential, the charge transfer to the catalyst and a decrease in binding energies of all catalyst components (Co, Mn, Al and O). Pilot plant verification of N₂O decomposition over K-promoted Co₄MnAlO_x is shown.

Key words: N₂O decomposition, Alkali metal, Promoter, Cobalt oxide, Layered double hydroxide

29 1. Introduction

30 Catalytic decomposition of N₂O belongs to the Best Available Technologies for N₂O
31 abatement from nitric acid production, which has been recognized as the biggest industrial
32 source of N₂O emission [1]. Many efforts have been made to develop the catalyst for efficient
33 nitrous oxide removal from nitric acid tail gases at economically appealing low temperature
34 (below 400 °C). However, this issue still remains an unsolved problem due to the presence of
35 inhibiting co-reactants in the feed gas (O₂, H₂O and NO_x) and the low concentration of the
36 N₂O pollutant.

37 Among tested catalysts, cobalt spinels such as Co₃O₄ [2-5] and calcined layered
38 double hydroxides (LDHs) containing cobalt Co-Al [6], Co-Mg-Al [7] Co-Rh-Al [7-8] and
39 Co-Mn-Al [9] are very promising. Our recent effort to improve the catalytic performance of
40 calcined Co-Mn-Al LDH (molar ratio Co:Mn:Al = 4:1:1) led us to the tuning of surface
41 properties by doping with different promoters like alkali (Li, Na, K), rare earth (La, Ce) and
42 noble metals (Pd, Pt) [10]. Among them, alkali promoters Na and K improved N₂O
43 conversion considerably [11] and a detail study of potassium effect in calcined Co-Mn-Al
44 layered double hydroxide on the catalytic decomposition of N₂O was carried out in our
45 previous work [9]. Similarly, such beneficial effect of alkali addition on N₂O decomposition
46 was observed for other cobalt spinel catalysts [12-17] as well as for CuO [18] and NiO [19].
47 Direct correlation between the activity in N₂O decomposition and spinel work function of K-
48 promoted Co-Mn-Al mixed oxide [20] and Li-, Na-, K- and Cs- promoted Co₃O₄ led to the
49 conclusion that alkali metals promotional effect is of electronic nature and is accompanied by
50 lowering of the spinel work function caused by the surface alkali adspecies. The sequence of
51 the promotional effect: undoped ≈ Li << Na < K < Cs-doped Co₃O₄ catalyst was published by
52 Kotarba group for N₂O decomposition in dry and wet gas [12].

53 Based on the published results, we suppose that the modification of Co-Mn-Al mixed
54 oxide by heavier alkali dopants, Rb and Cs, could result in obtaining even more active
55 catalysts than in the case of doping with K and Na. The aim of the present study is to compare
56 the alkali promotion effect at the same atom number of individual alkali metals in Co-Mn-Al
57 mixed oxide. For this reason, the constant molar ratio M/Co (M – alkali metal) was adjusted
58 as 0.037. Such level of alkali doping was previously found to be optimal for the K modified
59 Co-Mn-Al mixed oxide catalyst [9]. According to the work [12] published recently, the
60 higher cation radius of alkali metal atom directly influenced the value of the produced surface
61 dipole moment resulting in a proportional lowering of catalyst work function and which
62 causes an increase in catalytic activity upon alkali promotion at the same surface coverage.

63 Based on this theory, we expected that at the same atom number of individual alkali metals,
64 the catalytic activity will increase with ionic radius of alkali metals.

65 In presented contribution, Co-Mn-Al mixed oxide (molar ratio Co:Mn:Al = 4:1:1)
66 modified by the same molar content of Li, Na, K, Rb and Cs was prepared and AAS,
67 SEM/EDX, N₂ physisorption, XRPD, XPS, TPR-H₂, and TPD (CO₂, NH₃) were used for
68 characterization of the prepared materials. Evaluation of catalytic efficiency for the low
69 temperature N₂O catalytic decomposition in simulated waste gas from nitric acid production
70 (in the presence of O₂, H₂O and NO_x) to choose promoter for practical application in HNO₃
71 plant is provided.

72

73 **2. Experimental**

74

75 *2.1 Catalysts preparation*

76 The Co-Mn-Al layered double hydroxide precursor with Co:Mn:Al molar ratio of 4:1:1
77 was prepared by coprecipitation of corresponding nitrates with a solution of Na₂CO₃ and
78 NaOH at pH 10. The precipitated solid was subsequently washed, dried and calcined at
79 500 °C in air. More information on the synthesis procedure is mentioned in [21]. The obtained
80 catalyst was labeled as Co₄MnAlO_x.

81 Samples modified with alkali promoters were prepared by pore-filling impregnation
82 method (also termed as dry impregnation, impregnation to incipient wetness or capillary
83 impregnation). The support was contacted with a alkali nitrate solution of appropriate
84 concentration, corresponding in quantity to the total known pore volume or slightly less. The
85 concentrations of alkali solutions were adjusted to achieve the 3·10⁻⁴ mol alkali metal/g of
86 catalyst (molar ratio of alkali metal/Co = 0.037).

87

88 *2.2 Catalysts characterization*

89 The chemical composition of the prepared catalysts was determined by atomic
90 absorption spectroscopy (AAS) method using a Spectr AA880 instrument (Varian) after
91 dissolving the samples in hydrochloric acid.

92 The catalysts morphology and composition was investigated by a Philips XL 30
93 (25 keV) scanning electron microscope equipped with secondary electrons detector, back
94 scattered electrons detector and energy dispersion analyzer (SEM/EDX). Prior to the
95 SEM/EDX observations, the samples were coated with Au and Pd in the Ar flow.

96 The surface areas of the prepared catalysts were determined by N₂
97 adsorption/desorption at -196 °C using an ASAP 2010 instrument (Micromeritics, USA) and
98 evaluated by BET method. Prior to the measurement, the samples were dried at 120 °C for at
99 least 12 h.

100 The X-ray powder diffraction (XRPD) patterns were recorded under CoK α irradiation
101 ($\lambda = 1.789 \text{ \AA}$) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a
102 fast position sensitive detector VÅNTEC 1. Measurements were carried out in the reflection
103 mode, powder samples were pressed in a rotational holder, goniometer with the Bragg-
104 Brentano geometry in 2θ range from 5 to 80°, step size 0.02°. Phase composition was
105 evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data). The
106 crystallite size was calculated according to the (311) Co-Mn-Al spinel diffraction peak using
107 the Scherrer formula and lanthanum hexaboride (LaB₆) was used as a standard.

108 The X-ray photoelectron spectra (XPS) of the catalysts were measured on a Prevac
109 photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer.
110 The studied samples were loaded through a load lock (where pressure better than $3 \cdot 10^{-7}$ mbar
111 was achieved) into an ultrahigh vacuum analytical chamber with the base pressure of $5 \cdot 10^{-9}$
112 mbar. XPS measurements were taken with a monochromatized aluminum source AlK α
113 (E=1486.6 eV) and a low energy electron flood gun (FS40A-PS) to compensate charge on the
114 surface of nonconductive samples. Peaks were recorded with constant pass energy of 100 eV
115 for the survey and high resolution spectra. The binding energies were referenced to the C 1s
116 core level (284.6 eV) from hydrocarbon contaminations. The composition and chemical
117 surrounding of sample surface were investigated on the basis of the areas and binding
118 energies of Na 1s, K 2p, Rb 3d, Cs 3d, Mn 2p, Co 2p, O 1s, Al 2p and C 1s photoelectron
119 peaks. Fitting of the high resolution spectra was provided through the CasaXPS software.

120 Temperature programmed reduction (H₂-TPR) measurements of the calcined samples
121 (0.025 g) were performed using a system described in details in [22], with a H₂/N₂ mixture
122 (10 mol% H₂), flow rate 50 ml/min and the linear temperature increase of 20 °C/min up to
123 1000 °C. A change in H₂ concentration was detected with a mass spectrometer Omnistar 300
124 (Pfeiffer Vacuum).

125 Temperature programmed desorption (TPD) of NH₃ and CO₂ was carried out to
126 examine acid and basic properties of catalysts surface, respectively. 0.05 g of catalyst was
127 used for TPD experiments in the temperature range of 20–500 °C with the heating rate of
128 20 °C/min. Adsorbing gases were NH₃ and CO₂, helium was used as a carrier gas. Detailed
129 information about TPD experiments are presented in [22].

130

131 2.3 Catalytic measurements of N_2O decomposition

132 N_2O catalytic decomposition was performed in an integral fixed bed stainless steel
133 reactor of 5 mm internal diameter in the temperature range from 300 to 450 °C and
134 atmospheric pressure. The feed introduced to the reactor contained 0.1 mol% N_2O in helium.
135 Oxygen (5 mol%), water vapor (3 mol%) and NO (0.02 mol%) were added to some
136 experimental runs. The catalyst bed contained 0.1 g or 0.3 g of the sample with a particle size
137 of 0.160 – 0.315 mm. The space velocity WHSV of 20 000 or 60 000 $l\ h^{-1}\ kg^{-1}$ was applied.
138 The catalytic tests were performed under kinetic region [23]. The steady state of the N_2O
139 concentration level was measured. The quadruple mass spectrometer RGA 200 (Stanford
140 Research Systems, Prevac) was used for N_2O analysis ($m/z = 44$). Argon was used as internal
141 standard to eliminate instability of MS signal. The absolute error of N_2O conversion X (%)
142 evaluated from repeated catalytic runs was $X \pm 4$ (%).

143

144 3. Results and discussion

145

146 3.1 Characterization of the catalysts

147

148 3.1.1 Chemical composition and specific surface area

149 Chemical composition of alkali promoted Co_4MnAlO_x mixed oxide determined from
150 chemical analysis and SEM/EDX are summarized in Table 1. The alkali content in the
151 catalysts as well as alkali metal/Co molar ratio determined by AAS corresponded well to the
152 value adjusted in alkali nitrate solution during impregnation. Higher Na concentration found
153 in the Na modified sample was related to the presence of residual sodium ions from
154 coprecipitation procedure. The SEM/EDX analyses (not shown) documented nearly the same
155 morphology of the all prepared catalysts and quite homogeneous promoter distribution on the
156 catalysts' surface. No substantial changes of specific surface areas were observed after
157 impregnation of Co_4MnAlO_x mixed oxide by alkali metals (Table 2).

158

159 3.1.2 XRPD analysis

160 A well-crystallized hydrotalcite-like phase with slight amount of $MnCO_3$
161 (rhodochrosite) admixture was found in the XRPD pattern of the prepared Co-Mn-Al LDH
162 precursor (not shown) as it was reported also formerly [9, 21]. XRPD patterns of the alkali
163 promoted Co_4MnAlO_x mixed oxides prepared by impregnation of this precursor are presented

164 in Fig. 1. The Co-Mn-Al mixed oxide with spinel structure (S) was found in all catalysts. We
165 can assume that the impregnation of the Co-Mn-Al spinel samples by alkali metals caused
166 increase of crystallinity of the treated samples, probably due to the repeated calcination after
167 impregnation procedure. It is evident from the intensity increase of the characteristic
168 diffraction peaks of the spinel. However, the content of alkali metals did not significantly
169 influence crystallite size and the lattice d-spacing values of 311 of the Co-Mn-Al spinel (see
170 Table 2). In our recent publication [10], a slight decrease in the lattice parameter a in the case
171 of $\text{Co}_4\text{MnAlO}_x$ modified by lithium (0.1 – 1.5 wt%) was observed, which was caused by
172 diffusion of Li cations into the spinel lattice. In comparison with heavier alkali metal ions,
173 Na^+ , K^+ , Cs^+ and Rb^+ , Li^+ cation is too small and it was incorporated to the spinel octahedral
174 sites [12]. In present work, this decrease was not observed probably due to the low Li content.

175 Two catalysts, $\text{K}/\text{Co}_4\text{MnAlO}_x$ and $\text{Cs}/\text{Co}_4\text{MnAlO}_x$, were found to contain other
176 phases. The diffraction lines at d values of 0.386 nm and 0.193 nm in $\text{K}/\text{Co}_4\text{MnAlO}_x$ XRPD
177 pattern can be assigned to KNO_3 and/or peroxide K_2O_2 . Presence of undecomposed KNO_3
178 after calcination procedure is questionable since according to Shen et al [24, 25], KNO_3 began
179 to decompose in the range of 127 to 227 °C upon loaded on inorganic supports resulting from
180 a special interaction between KNO_3 and the surface of porous materials, i.e. at much lower
181 temperatures than unsupported KNO_3 (650 °C [26]) and also at lower temperature than our
182 calcination temperature was. Birnessite-type oxide, K_xMnO_2 , detected in Co-Mn-Al mixed
183 oxide modified by 3 wt% K previously [9] was not observed here probably due to lower
184 potassium content. Quartz (Q) was detected in the sample $\text{Cs}/\text{Co}_4\text{MnAlO}_x$, which was caused
185 by a contamination of the sample with laboratory glass during the preparation procedure. The
186 other nitrate treated $\text{Co}_4\text{MnAlO}_x$ mixed oxides were not found to contain nitrite or oxide of
187 the given alkali metals Li, Na and Rb.

188

189 3.1.3 XPS analysis

190 XPS data provide information about the content and chemical state of the elements in
191 the near-surface region obtained from core photoemission intensity data. Binding energies
192 (BE) of the selected photoemission lines of catalysts are summarized in Table 3, the XPS
193 spectra of Co 2p, Mn 2p, Al 2p and O 1s electrons are depicted in Fig. 2 and the XPS spectra
194 of Na 1s, K 2p, Rb 3d and Cs 3d are shown in Supplementary data.

195 The detailed XPS analysis of Co-Mn-Al mixed oxide (4:1:1) without alkali promoters,
196 based on the comparison of catalyst and appropriate oxide standards, was published in our
197 previous work [27]. The results of XPS analysis of the $\text{Co}_4\text{MnAlO}_x$ mixed oxide in this work

198 correspond well with those published results. Presence of Co^{2+} (component with lower BE)
199 and Co^{3+} (component with higher BE) is recognized from Co 2p electron spectra of
200 $\text{Co}_4\text{MnAlO}_x$ as well as of alkali modified $\text{Co}_4\text{MnAlO}_x$. Identification of cobalt chemical state
201 is based on two facts: (i) satellite lines are of relatively poor intensity, (ii) the values of spin-
202 orbital splitting [27]. An decrease in the $\text{Co}^{2+}/\text{Co}^{3+}$ surface molar ratio is observed after alkali
203 introduction. However, no straight correlation between kind of alkali promoter and this trend
204 can be found.

205 Oxygen is present in several chemical states in all samples. The prevailing state is that
206 with the lowest binding energy belonging to oxide form, while the spectra component with
207 higher binding energy can be attributed to $-\text{OH}$, $\text{C}=\text{O}$ and CO_3^{2-} groups [28] or to non-
208 stoichiometric spinel like phase [29]. Oxygen with the highest binding energy could be
209 assigned to $\text{C}-\text{OH}$, COO^- groups [28] or adsorbed oxygen [29].

210 To identify the oxidation state of manganese, O 1s (the component with the lowest BE)
211 to Mn $2p_{3/2}$ peak separation was used [27]. Two chemical states, Mn^{3+} and Mn^{4+} were
212 identified in all alkali modified $\text{Co}_4\text{MnAlO}_x$ catalysts. An increase in value of Mn $2p_{3/2}$ - O 1s
213 was observed after alkali introduction.

214 Lithium was not detected on the catalyst surface by XPS due to the incorporation to the
215 spinel lattice [10, 12]. BE value of Na 1s 1071.3 eV corresponded well with the value
216 obtained by Yoshida for Na impregnated titanate nanobelt (1071.3 eV) [30]. BE of K $2p_{3/2}$
217 was observed similarly as in our recent work [9]. BE of Cs $3d_{5/2}$ had similar value as Cs
218 supported on Zr-Cr spinel (724.7) [31] or on Co_3O_4 (724.6 eV) [32].

219 Compared to non-modified $\text{Co}_4\text{MnAlO}_x$ mixed oxide, the presence of alkali metals
220 caused the decrease of BE for Co, Mn, Al and O component with the lowest BE (oxide form).
221 It indicates an increase of electron density and a change in the electronic state of metals to the
222 lower valence state [33]. This trend can be interpreted as electron donation from alkali cations
223 to oxygen anions surrounding and further charge transfer towards cobalt, manganese and
224 aluminium [14].

225 Co:Mn:Al molar ratios calculated from XPS and SEM/EDX (Tab. 1) show significant
226 enrichment of the surface by Al. Similar enrichment of the surface by Al was observed
227 recently in the calcined hydrotalcites Co-Al [29], Cu-Mg-Al [34], Co-Mn-Al [9, 27] and Ni-
228 Al [35]. Relation between bulk and surface alkali metal/cobalt molar ratio showed that
229 concentration of alkali metals on the surface is higher than in the bulk. Similar enrichment of
230 surface by alkali metals was observed for Co-Mn-Al oxide and potassium [9], for ZnO and
231 potassium [36] or for titanate nanobelt and sodium [30]. In the case of cesium, a very high

232 enrichment in Cs concentration on the catalyst surface was observed. We suppose that all
233 alkali promoters with exception of Li are located on the catalyst surface because of the
234 impregnation method used and the impossibility of their diffusion into the spinel lattice due to
235 the big ionic radius.

236

237 3.1.4 H₂-TPR

238 H₂-TPR is a simple and effective tool to evaluate reducibility of catalysts and the
239 mobility of oxygen. Fig. 3 compares H₂-TPR profiles of the Co₄MnAlO_x catalyst with
240 different alkali promoters. Reduction of catalysts proceeds in two temperature regions. In the
241 low-temperature region, reduction of Co³⁺ → Co²⁺ → Co⁰ [37-41] and Mn⁴⁺ → Mn³⁺
242 proceeds [42, 43]. High-temperature peak can be attributed to the simultaneous reductions of
243 Mn₂O₃ and Mn₃O₄ [44] and to reduction of spinel-like phases.

244 Presence of cations (K, Ca, Mg) in the Co and Mn oxides shifted the temperature
245 maxima to lower values [14, 45], similarly as in our measurements. Hydrogen consumption
246 and temperature of reduction peaks maxima are summarized in Table 4. Modification of
247 Co₄MnAlO_x mixed oxide by alkali promoters caused decrease of hydrogen consumption
248 probably connected with the increase of electron density and the change in the electronic state
249 of cobalt and manganese to the lower valence state as was observed from XPS. Moreover,
250 shift of the low temperature peak to the lower temperature observed in the order Na > K > Rb
251 > Cs documented changes in reducibility and metal-oxygen bond strength.

252

253 3.1.5 NH₃-TPD and CO₂-TPD

254 As expected, modification of Co₄MnAlO_x surface by alkali promoters influenced acid-
255 base properties of catalysts surface (Fig. 4, 5, Table 4). Amount of weak acid surface centers
256 (determined as NH₃ consumption in temperature region of 25 – 500 °C) decreases in the
257 order: Cs < Rb < K ≈ Na < Li < Co₄MnAlO_x while the amount of weak basic centers
258 (determined as CO₂ consumption in temperature region of 25 – 500 °C) in the same order
259 increases (Fig. 6).

260

261 3.2 N₂O catalytic decomposition

262 Figure 7 shows the temperature dependences of the N₂O conversion over alkali
263 promoted Co₄MnAlO_x mixed oxide in inert gas. According to our hypothesis, catalysts
264 modified with Cs and Rb were the most active followed by K, Na and Co₄MnAlO_x.

265 Modification of $\text{Co}_4\text{MnAlO}_x$ by Li caused a decrease in N_2O conversion in accordance with
266 our results published in [10,11].

267 N_2O catalytic decomposition in the presence of other gaseous components is depicted in
268 Fig. 8. Very slight inhibition by oxygen (comparable with experimental error) was observed
269 over the catalysts contained Cs, K, Rb and over the non-modified $\text{Co}_4\text{MnAlO}_x$ mixed oxide,
270 while the higher decrease of N_2O conversion in the presence of O_2 was found out over the
271 catalysts contained Na and Li. Generally, the oxygen inhibition of N_2O catalytic
272 decomposition is connected with an ability of catalyst surface to adsorb oxygen from the gas
273 phase and/or with a degree of oxygen surface coverage. If no oxygen inhibition is observed
274 after the O_2 addition to the reaction mixture, it means that oxygen is not being adsorbed on the
275 catalyst surface or the catalyst surface has been already covered by oxygen during the N_2O
276 decomposition in inert. This oxygen can come from dissociation of N_2O molecule or it can be
277 the readsorbed O_2 from gas phase at high N_2O conversions. Our recent TPD- O_2 experiments
278 showed that O_2 inhibition over the Na- and Li- containing catalysts can be explained by the
279 O_2 adsorption from gas phase while high oxygen surface coverage during N_2O decomposition
280 in inert gas is the reason of almost no O_2 inhibition over K-containing and non-modified
281 $\text{Co}_4\text{MnAlO}_x$ [10, 11].

282 Excellent results were obtained for N_2O catalytic decomposition in the mixture
283 containing oxygen and water vapor over Cs-promoted $\text{Co}_4\text{MnAlO}_x$ while only slight
284 inhibiting effect was observed in the presence of other alkali modified catalysts with
285 exception of Li. The inhibiting effect of water vapor for oxide catalysts can be rationalized
286 primary in terms of blocking of surface active centers by water adsorption [46].

287 The same activity order as for N_2O decomposition in inert gas was observed also in
288 simulated waste gas from nitric acid production containing oxygen, water vapor and nitrogen
289 oxides. However, inhibition by NO_x was observed for catalysts modified by Na, K and Cs.
290 This is in good agreement with our results published previously for K-promoted $\text{Co}_4\text{MnAlO}_x$
291 [9, 10]: potassium (and generally alkali metals) promoter suppresses water inhibition effect
292 significantly while extent of NO_x inhibition is dependent on acido-basic properties of catalyst
293 surface. This finding has very important practical meaning as it implies that suitable position
294 of alkali modified $\text{Co}_4\text{MnAlO}_x$ catalyst in a HNO_3 plant is downstream the SCR NO_x/NH_3
295 unit where NO_x concentration is low.

296 For practical application, the catalyst stability is also important besides sufficient
297 activity. Taking into account the already known volatility and surface mobility of alkali
298 promoters, the surface composition of Rb- and Cs- containing catalysts after catalytic

299 experiments (approximately 30 hours) were verified by XPS. When we analyzed data in both
300 tables presenting the XPS results (Table 1 and 3), we should conclude that the surface of Rb-
301 and Cs-promoted samples changed during the catalytic tests. However, the nature of these
302 changes is different in both cases.

303 For the Rb-doped one, obviously oxidation of Co^{2+} to Co^{3+} connected with reduction of
304 manganese cations is observed. The oxidation of Co is mainly manifested by changes in peak
305 areas related to both kinds of Co ions (from 1.47 to 1.15), whereas the reduction of Mn by
306 decrease in Mn $2p_{3/2}$ - O 1s distance.

307 On the other hand, in the Cs-containing catalyst segregation of Co phase occurred. The
308 surface was enriched in Co (compare the results presented in Table 1). The migration Co
309 oxide to the outermost part of surface resulted in a shift in O 1s and Co $2p_{3/2}$ peaks and
310 probably Al 2p, Cs $3d_{3/2}$ and Cs $3d_{5/2}$.

311 Rubidium and especially cesium exhibited very interesting promoting effects which
312 predetermine them for the preparation of efficient industrial catalysts. The work on optimizing
313 Cs loading on the $\text{Co}_4\text{MnAlO}_x$ catalysts has been commenced and the obtained results will be
314 the subject of our next paper.

315 Based on our previous work devoted to potassium promoter where not only high
316 activity [9] but also long term stability was verified [10] and due to the lower price of K
317 compared to Cs salts, we chose $\text{Co}_4\text{MnAlO}_x$ mixed oxide with potassium promoter for the
318 production of our first industrial scale catalyst. It was found out that the Co-Mn-Al mixed
319 oxides with 1.1-1.8 wt% K were the most active in the N_2O decomposition. The catalytic
320 activity increased with increasing potassium content up to the optimum value; the further
321 increasing K content resulted in gradual decrease of N_2O conversion [20]. Content of
322 potassium was set as 2 wt%, which was determined as optimal amount for the high N_2O
323 conversion in the presence of oxygen and water vapor [9]. In nowadays, the prepared pilot
324 plant K/Co-Mn-Al mixed oxide catalyst (cylinder 5x5 mm) K is tested in real waste gas from
325 nitric acid plant production in pilot plant unit situated downstream SCR NO_x/NH_3 . In Fig. 9
326 the stability of catalyst is shown. It is evidence that catalyst demonstrates N_2O conversion of
327 approximately 80% for more than 50 days. Result is comparable with N_2O conversion
328 calculated according to the model of fixed bed catalytic reactor for N_2O abatement in waste
329 gas from HNO_3 published in our recent work [47].

330 Although our research is focused on the development of catalyst for N_2O
331 decomposition in the waste gas from nitric acid production, this method could be used also for
332 N_2O abatement in other waste gases. In this case, the effect of other presented components

333 like SO₂, CO₂, CO has to be tested e.g. for the application of the gas cleaning from fluidized
 334 bed combustion where N₂O concentration of 50-500 ppm are presented [48].

335

336 **3.3 Effect of the alkali cation promoters**

337 The decomposition of N₂O over alkali promoted Co₄MnAlO_x mixed oxides proceeds
 338 via cationic redox mechanism as was confirmed by direct correlation between the surface
 339 work function value of the K-promoted Co₄MnAlO_x catalysts and their catalytic activity [20]
 340 and as was also suggested for similar system of K, Zn-promoted Co-containing spinel-type
 341 catalyst [49]. In this mechanism, transition metal ions act as surface electron donor centers
 342 stimulating the transfer of electron density for activation of the N₂O molecule and further as
 343 electron acceptor centers of the resultant surface O⁻ intermediates. This finding is in
 344 agreement with elementary steps of N₂O decomposition proposed over the Co-Mn and Co-La-
 345 Al mixed oxide prepared from LDH precursor (Eq. 1-3) [50, 51].



349 The mechanism of the interaction between N₂O and the catalysts active centers is
 350 generally thought to be a charge donation from the catalyst to the antibonding orbitals of N₂O,
 351 which destabilizes N-O bond and this leads to its scission [48]. Therefore, electron charge
 352 transfer from the metal ion to the N₂O molecule is a crucial step for N₂O decomposition.
 353 Electron transfer occurs from low oxidation state metal cations, which then increases their
 354 oxidation state. The reduction of the ion to a low oxidation state is a subsequent, very
 355 important step for the regeneration of the active centers [13].

356 Accordingly, the activity of the Co₄MnAlO_x mixed oxides is attributed to the
 357 coexistence of a Co²⁺-Co³⁺ and Mn³⁺-Mn⁴⁺ ion pairs because of a facile one-electron transfer
 358 between these ions during N₂O decomposition. The increase in electron density of Co²⁺ and
 359 Mn³⁺ sites (observed from XPS) due to doping of alkali metals is proportional to decrease of
 360 ionization potentials of alkali metals. The increase in electron density of Co²⁺ and Mn³⁺
 361 makes them more readily to donate electrons to the N₂O and thus facilitates the activation of
 362 N₂O and its cleavage (Eq. 1). Moreover, modification by alkali metals also cause differences
 363 in reducibility of catalysts as determined from H₂-TPR. Because the decomposition of N₂O
 364 was conducted to a temperature 450 °C, only species reduced in 1st TPR peak (*T*_{max} around
 365 400 °C) are considered to be involved in reaction. An increase in N₂O conversion with the

366 decrease of 1st peak temperature maxima was observed (Fig. 10). This shift can be interpreted
367 as easier reducibility of Co^{3+} and Mn^{4+} connected with the weakening their bonds with
368 oxygen, thus increased surface oxygen mobility and facilitates the oxygen desorption from
369 catalyst surface (Eq. 2), similarly as observed elsewhere [14, 52]. $\text{Co}_4\text{MnAlO}_x$ and
370 $\text{Li}/\text{Co}_4\text{MnAlO}_x$ catalyst was not included into this correlation because of Li entering into the
371 crystal lattice of transition mixed oxides. From Fig. 11 we can see that the high N_2O
372 conversion in simulated waste gas is connected with the high amount of basic sites and the
373 low amount of acid sites. This correlation is valid only for studied $\text{Co}_4\text{MnAlO}_x$ modified with
374 the same amount of alkali metals and cannot be considered as general. No dependency of
375 catalytic activity on acido-basic surface properties has been found for other catalytic systems
376 according to our knowledge. Therefore, we believe that the acid-base properties are not
377 critical to the activity of the catalyst in contrast to their reducibility.

378 The proposed elucidation of alkali metals promotional effect at the same coverage on
379 $\text{Co}_4\text{MnAlO}_x$ mixed oxides due to easy surface ionization of alkali metals, charge transfer to
380 the catalyst surface and decrease in binding energies of all components (Co, Mn, Al and O) is
381 in good agreement with promotional effect order $\text{Na} < \text{K} < \text{Cs}$ in Co_3O_4 [12]. It corresponds to
382 the lowering of the spinel work function, which is proportional to the surface dipole moment
383 gauged by the ionic radius of alkali cations ($\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$).

384

385 4. Conclusions

386 The promotional effect of alkali promoters (Li, Na, K, Rb and Cs) on $\text{Co}_4\text{MnAlO}_x$
387 mixed oxide activity in N_2O decomposition was investigated by reactivity steady state
388 experiments in inert and simulated waste gas combined with AAS, SEM/EDX, N_2
389 physisorption, XRPD, XPS, H_2 -TPR and TPD measurements. The sequence of the
390 promotional effect: $\text{Li} < \text{undoped} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ -doped catalyst was explained in terms
391 of charge donation from formed alkali metal cations to oxide form of surface oxygen and
392 further to cobalt and manganese. Obtained experimental data confirmed the theory that the
393 catalytic activity will increase with the increasing ionic radius of alkali metals at the same
394 surface coverage.

395 Potassium and cesium can be chosen as suitable promoters of $\text{Co}_4\text{MnAlO}_x$ mixed oxide
396 for N_2O abatement in HNO_3 waste gases. Cesium was selected for the highest activity in wet
397 waste gas for further detail investigation, whereas potassium was selected due to its lower
398 price compared to Cs salts and our recent work dealing with optimization of potassium
399 content for scale up. The test in pilot plant unit over Co-Mn-Al mixed oxide promoted with 2

400 wt% of K showed that this catalyst is active and stable in the real waste gas from the nitric
401 acid production.

402

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